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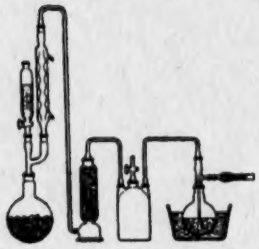

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JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume 16, Number 1 January-February, 1961

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A METHOD FOR THE MICROPHOTOMETRIC TITRATION OF MATERIAL IN ULTRAVIOLET LIGHT IN WHICH THE END POINT IS RECORDED

COMMUNICATION I. THE DESIGN OF A MICROTITRATOR AND THE DETERMINATION OF IRON CONTENT

K. P. Stolyarov, N. N. Grigor'ev, and Ch'en Kuo-Liang

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Recently, microchemical methods for the quantitative determination of materials (particularly titrimetric methods) have found wide application. The main disadvantage of microtitrimetric determinations is the relatively large indicator error. A large number of titration methods which do not involve the use of indicators (amperometry, potentiometry, etc.) and which are based on the use of the usual type of apparatus, but with smaller absolute volumes of the test material, have been suggested in order to eliminate this indicator error. Nevertheless, the complexity of the apparatus and the large number of factors which affect the experimental results have hindered the wide application of these methods in microchemical practice.

Earlier [1], one of the authors of the present article suggested a visual method for the titration of materials without an indicator in ultraviolet light. The method is fairly simple and effective. The method can be widely used for microtitrimetric determination of materials with variable valence. In combination with various masking methods (e. g., complexonometric), and by using special organic reagents, this method can be used for the determination of elements with a constant valence (in precipitation and neutralization methods, and in others).

Normal microchemical methods permit, as a rule, the determination of the content of a component in very small amounts of test material, in those cases where the latter contains a high content of the component to be determined (sometimes up to 90-100%). The method suggested is applicable in those cases where the absolute content of the test component in microsamples amounts to a fraction of a percent. Under these conditions the relative error does not exceed 0.5-2.0%. There is no need to carry out complex calculations of the titration errors.

Microchemical photometric titration in ultraviolet light is carried out by means of a specially constructed microtitrator which ensures an objective recording of the end point.

Microtitrator design. The apparatus is shown schematically in Fig. 1. Light from an ultraviolet radiation source 1 (a PRK-4 tube) is split into two beams: the analytical and compensating beams. The analytical beam passes through a light filter 6, the cuvette with the material to be titrated 5, a variable slit 4, a luminescent screen 3, and a receiver for the radiation 2. The compensating beam passes through a light filter 6', a variable slit 4', and a receiver for the radiation 2'. The photocurrent is recorded by means of a mirror galvanometer 7, which is connected through a resistance 8 and a shunt resistance 9. The light filter 6 used is a Mark UFS-3 light filter, whose transmission curve is shown in Fig. 2. The titration cuvette is a vessel with plane parallel sides and with capacity of 3-4 ml; it is made from ordinary optical glass, which readily passes ultraviolet radiation with a wavelength of 365 mμ. The slits 4 and 4' are designed for arbitrarily changing the value of the light beam. The

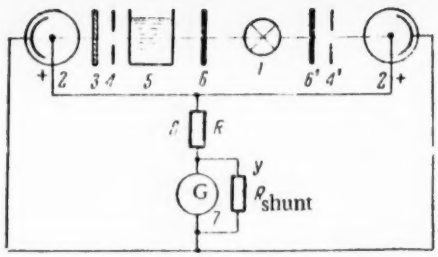

Fig. 1. Schematic diagram of the microtitrator. 1. Ultraviolet radiation source; 2,2') photoelements; 3) luminescent screen; 4,4') variable slits; 5) cuvette containing the material to be titrated; 6,6') light filters; 7) mirror galvanometer; 8) resistance; 9) shunt.

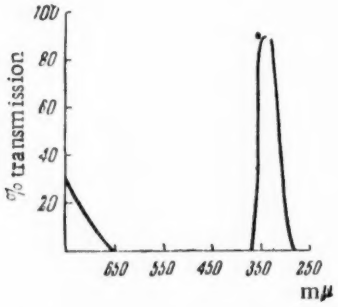

Fig. 2. Transmission curve of the UFS-3 light filter.

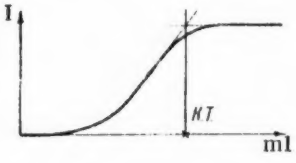

Fig. 3. Titration curve.

TABLE 1

Fe, mg			Fe, mg		
taken	found	absolute error	taken	found	absolute error
6.27	6.25	—0.02	3.58	3.60	+0.02
6.27	6.25	—0.02	2.23	2.25	+0.02
5.33	5.35	—0.03	2.23	2.22	—0.01
5.33	5.35	—0.03	1.15	1.13	—0.02
4.48	4.48	0	1.15	1.14	—0.01
4.48	4.46	—0.02	0.38	0.39	+0.01
3.58	3.57	—0.01	0.38	0.40	+0.02

TABLE 2

HCl conc., N	Fe, mg		
	taken	found	absolute error
0.2	2.87	2.89	+0.02
0.2	2.87	2.86	—0.01
0.4	2.23	2.25	+0.02
0.4	2.23	2.25	+0.02
0.8	2.87	2.86	—0.01
0.8	2.87	2.89	+0.02

radiation receivers are selenium photoelements with a maximum sensitivity at 580 mμ. Accordingly, in order to increase the sensitivity of the apparatus we introduced a luminescent screen 3 in order to convert the ultraviolet radiation into visible radiation; the screen was made from uranium glass or any other luminescent material. The light filter 6' is chosen so that its maximum transmission is near the maximum sensitivity of the photoelement.

The apparatus is connected into a compensation scheme, while the photoelements are irradiated from one light source; accordingly, when the parameters of the photoelements are correctly chosen there is no need for a particularly careful stabilization of the ultraviolet radiation source.

The test material which absorbs ultraviolet radiation is introduced into the cuvette. The intensities of the two light beams (4,4') are equated (the galvanometer reading should be zero), and titration carried out with known portions of working solution.* The changes of the photocurrent with the amount of reagent added are recorded, and a curve plotted within the coordinates: volume (in ml) of titrant – galvanometer reading. The end point is determined graphically. A typical titration curve is shown in Fig. 3. It is sufficient to obtain a few points on the linear section of the left hand side of the curve and a few points on the right hand side (where the galvanometer reading is constant). This enables the time taken to carry out a titration to be cut down appreciably without affecting the final results.

*The working solution (titrant) is introduced into the cuvette containing the solution to be titrated by means of a microburet with a capacity of 2 ml and with scale divisions of 0.01 ml, the tip of the microburet being immersed in the solution; the microburet is provided with a pneumatic seal and a microscrew. The use of a similar type of buret, which has been described by us previously in [2], almost completely eliminates the drop error.

TABLE 3

Concentration	Fe, mg		
	taken	found	absolute error
0.8 $N H_2SO_4$	1.20	1.25	+0.05
0.4 $N H_2SO_4$	1.20	1.21	+0.01
0.6 $N HNO_3$	1.20	1.33	+0.13
0.6 $N HNO_3$	0.90	0.98	+0.08
0.6 $N HNO_3$	0.60	0.75	+0.15

TABLE 4

Fe taken, mg	Added, mg	Fe found, mg	absolute error, mg	Limiting ratio Fe : Me
	Co^{2+}			
2.23	29.45	2.24	+0.01	1 : 13
2.23	73.63	2.24	+0.01	1 : 33
2.23	117.90	2.25	+0.02	1 : 50
	Ni^{2+}			
2.87	5.86	2.87	0	1 : 2
2.87	88	2.90	+0.03	1 : 30
2.87	117.3	2.90	+0.03	1 : 40

TABLE 5

Sample wt., mg	Fe, mg		Fe content, %	
	added	found	found	specified content
0.4642	–	5.06	1.09	1.02
0.4776	–	4.86	1.02	1.02
0.4776	7.2	12.12	1.03	1.02

The technique used for determination of iron content. The method suggested for the iodometric microdetermination of iron is based on the well known reaction $2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$, the liberated iodine being titrated with sodium thiosulfate. The only component which absorbs in the working part of the spectrum (λ_{max} = 365 mμ) in this case is elementary iodine. Divalent iron in hydrochloric acid solution has an absorption band with an origin at 300 mμ, while potassium iodide absorbs about 250-280 mμ and sodium thiosulfate and sodium dithionate are also transparent in the spectral region chosen.

The iron content is determined as follows. To 2-3 ml of the test solution, which is a hydrochloric acid solution of a trivalent iron salt and which is contained in the titration cuvette, is added excess potassium iodide; after a certain time interval, sufficient for the reaction to go to completion, the apparatus is brought to the operating state, and the tip of the microburet containing the sodium thiosulfate solution introduced into the cuvette; the titrant is then added, with constant stirring, until the galvanometer readings do not change appreciably on adding the titrant; a titration curve is then constructed and the iron content determined graphically.

Table 1 contains the results for the determination of iron in 1 N hydrochloric acid.

The results given in Table 2 show the relation between the experimental results and the acidity of the solution.

It is evident from Tables 1 and 2 that determination of iron content by this method gives completely satisfactory results.

Sulfuric, nitric, and hydrochloric acids are most frequently used for dissolving test material; accordingly, we thought it would be of interest to study the effect of sulfuric and nitric acids on the results of iron determination.

It is clear from Table 3 that nitric acid affects the results to the greatest extent; this is, presumably, related to its oxodizing capacity. Cobalt and nickel do not interfere with the iron determination (Table 4).

Arsenic and copper, which themselves oxidize iodide to the elementary state, interfere with the iodometric determination of iron; tin, lead antimony, bismuth, and mercury also interfere. We removed these elements from solution by cementation on metallic aluminum; removal of the elements indicated is quantitative. Such a technique enables iron to be determined in materials containing relatively large amounts of the elements indicated.

TABLE 6

Sample wt., g	Fe found, mg	Fe content, %	
		found	specified content
0.3150	2.33	0.74	0.76
0.2716	1.91	0.71	0.76

TABLE 7

Expt. No.	Fe found, %	
	by the suggested method	by the dichromate method
1	4.31	4.42
2	4.28	4.42

Determination of the iron content of bronze. An aliquot of the test sample is dissolved by heating in nitric acid, concentrated sulfuric acid is added to the solution obtained, and the solution evaporated until sulfuric acid fumes appear. The sulfates are dissolved in water and hydrochloric acid is added. Cementation is then carried out on an accurately weighed amount of aluminum metal (0.4 g). Copper and other elements are removed by filtration. The solution obtained is evaporated to a small volume, the nitric acid is oxidized, and precipitation effected with ammonium hydroxide. The precipitate is dissolved in 1 N hydrochloric acid and the solution transferred to a 25 ml standard flask, in which it is made up to the mark with 1 N hydrochloric acid; the iron is determined in an aliquot of this solution as described above. In parallel, experiments are carried out with the same amount of aluminum. The results obtained are given in Table 5.

Determination of the iron content of a manganese concentrate. An aliquot of the concentrate is decomposed with concentrated hydrochloric acid, the solution obtained is neutralized with ammonia, and then some more hydrochloric acid added to establish a definite acidity. The solution obtained is transferred to a 25 ml standard flask, and its volume made up to the mark with distilled water. The iron content is determined on an aliquot of this solution (Table 6).

Determination of the iron content of an ore. An aliquot of the ore is decomposed by heating with aqua regia, the solution is evaporated to a small volume and 3 ml of concentrated sulfuric acid added; the solution is again evaporated until sulfuric acid fumes appear. The residue is dissolved in water, and, after filtering the solution, precipitation carried out with ammonium hydroxide. The washed hydroxide precipitate is dissolved on the filter in 1 N hydrochloric acid, and the filtrate transferred to a 25 ml standard flask. The iron content is determined on an aliquot of the solution. For comparison, iron was also determined by the dichromate method (Table 7).

SUMMARY

A method has been developed for the microphotometric titration of test materials in ultraviolet light, taking as an example the determination of iron. The relative experimental error is about 0.5%.

A description is given of the design of a microtitrator for carrying out microphotometric titration in ultraviolet light, the end point being recorded.

The method used for determining iron has been tested on samples of bronze, a manganese concentrate, and an ore.

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*Original Russian pagination. See C. B. translation.

N,N'-DI-(2-HYDROXY-5-SULFOPHENYL)-C-CYANOFORMAZINE AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF GALLIUM

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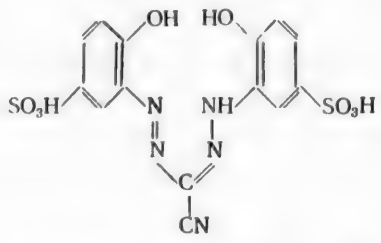
Formazine contains the tetrazo group: $Ar-N=N-C=N-NH-Ar$ in its molecule. Wizinger and co-workers [1-2] have synthesized a series of formazines. The most interesting formazines are those which contain carboxyl or hydroxyl groups in the ortho position to the tetrazo group, since they form complexes with five- or six-membered rings with metal ions. The substituent located on the meso carbon atom affects the properties of the compounds formed. Thus, compounds formed with formazines which contain the cyano group ($-N=N-\underset{\displaystyle CN}{\underset{|}{C}}=N-NH-$) in the meso position are characterized by their high stability towards acids.

The capacity of formazines to form complex compounds with metals has not yet been used sufficiently in analytical chemistry. The present article contains a description of a method for synthesizing N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine [1]* and it is shown that gallium can be photometrically determined by means of this reagent.



Synthesis of N,N'-di-(2-hydroxy-5-sulfophenyl)-C cyanoformazine. 6.0 g (0.031 mole) of 2-amino-1-phenol-4-sulfonic acid is suspended in 6 ml of concentrated hydrochloric acid, and is diazotized at room temperature with a solution of 3.0 g sodium nitrite in 10 ml of water. 3.4 g (0.032 mole) of sodium cyanoacetate is dissolved in 30 ml of a 20% sodium hydroxide solution, and is coupled at room temperature with the diazotized 2-aminophenolsulfonic acid. The solution is left overnight, after which it is acidified with glacial acetic acid until the red precipitate ceases to separate out. The latter is filtered off, dried in air on a porous plate, and recrystallized from dilute (1 : 1) ethanol. The product obtained is boiled for 10 min with glacial acetic acid, and again recrystallized from dilute ethanol, and dried at 120°. 2.9 g (36.1%) of the formazine is obtained in the form of its disodium salt. The fine brown-red, hygroscopic needles, which do not melt up to 250°, are readily soluble in water and ethanol, and are insoluble in ether, benzene, acetone, carbon tetrachloride, and chloroform. Acid solutions of the compound have an orange color, while alkaline solutions are violet in color.

Found %: N 14.16; 14.40; S 13.66; 13.25. $C_{14}H_9O_8N_5S_2Na_2$. Calculated %: N 14.43; S 13.20.

*This compound is mentioned in a review article [1], which also contains references to Swiss patents 245, 475 (July 16, 1945) and F. P. 930, 624 (July 16, 1946).

TABLE 1

The Reaction of N,N'-Di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine with Cations as a Function of the pH of the Medium

Element	pH at which the color of the formazine solution starts to change	Element	pH at which the color of the formazine solution starts to change
Copper	< 2.0	Vanadium (V)	2.2
Titanium	< 2.0	Uranium (VI)	3.0
Gallium	2.2	Iron (II)	3.0
Nickel	2.2	Iron (III)	3.0
Cobalt	2.2	Bismuth	3.5
Vanadium (III)	2.2	Tin (VI)	3.5
Zinc	4.0	Chromium (III)	5.0
Indium	4.0	Magnesium	5.0
Germanium	4.0	Calcium	5.0
Aluminum	4.5	Arsenic (III)	> 5.0
Lead	4.5	Arsenic (V)	> 5.0
Cadmium	4.5		
Manganese (II)	5.0		

Formazine forms soluble, colored compounds with metal ions. The color change of formazine solutions, which is determined by its interaction with cations, is most clearly expressed in acid media, in which the orange color of the formazine solution, in the presence of most cations, changes into blue or violet. Under such conditions, the color change of the solution in the presence of cations depends on the pH (Table 1).

Buffer solutions (acetate–hydrochloric) with pH intervals of 1 were used. The concentration of the cations in solution was about 0.001 M. The solutions were kept at room temperature for 20 hr. The color change of the solutions was observed visually.

It follows from the results given in Table 1 that at pH 3 a change in the color of the formazine solution is caused by only a small number of elements, in particular, gallium. In this connection we thought it would be of interest to test N,N'-di-(2-hydroxy 5-sulfophenyl)-C-cyanoformazine as a reagent for gallium, particularly in view of the fact that there is only a comparative small number of sensitive reagents possessing sufficient selectivity which are available for the determination of this element [3, 4].

A study of N,N' di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine as a reagent for gallium. The reaction of gallium with N,N'-di-(2-hydroxy-5-sulfophenyl)-C cyanoformazine (henceforth referred to as formazine) was studied in acetate-hydrochloric solutions; the pH was controlled by means of a glass electrode. Aqueous solutions of formazine were used in the course of the work; such solutions are completely stable for two weeks. Standard gallium solutions were prepared by dissolving chemically pure gallium metal in hydrochloric acid.

The light absorption of formazine and of its compound with gallium was studied within the pH range 2-7.5 on the SF-2M recording spectrophotometer in the wavelength range 400-700 mμ. Water (twice distilled) was used as the reference solution. Solutions with equimolar concentrations of gallium and formazine: [Ga] = [Formazine] = $= 2.2 \times 10^{-5}$ M were used in the experiments. The solutions were kept for two hours at 60° and then cooled to room temperature over an hour period. Results of the optical density measurements are given in Fig. 1. Over the pH range 2-4, the absorption band of the compound remains constant; at higher pH values it shifts to the shorter wavelength side, and the shape of the curves alters. This phenomenon would suggest the existence of at least two complex gallium compounds in the system.

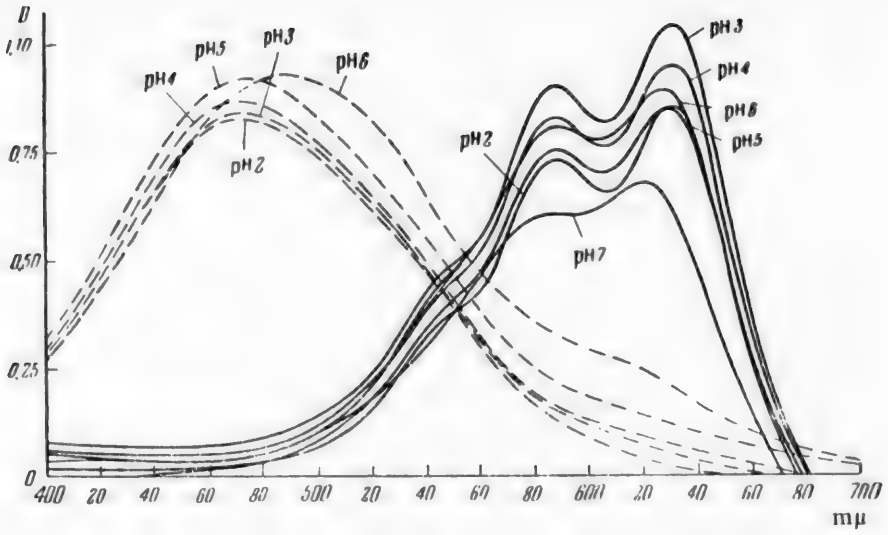


Fig. 1. Absorption curves of solutions of N,N'-di-(2 hydroxy-5-sulfophenyl)-C-cyanoformazine and of its compound with gallium. Solid lines) gallium compound: [Ga] = [formazine] = 2.2×10^{-5} M; dotted lines) formazine: 2.5×10^{-5} M; SF-2M spectrophotometer; l = 2 cm.

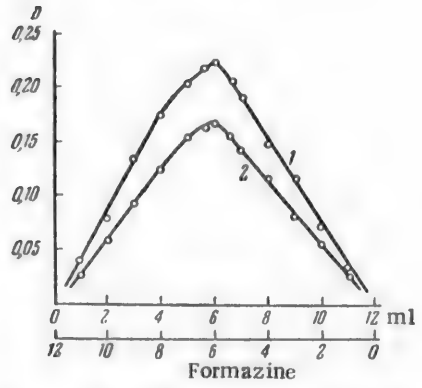


Fig. 2. Determination of the composition of the compound of gallium with N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine. 1) pH 3; 2) pH 6; SF-2M spectrophotometer; l = 2 cm; Σ Ga + formazine 5×10^{-6} M; λ = 634 mμ.

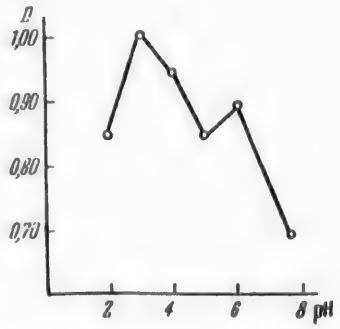


Fig. 3. The effect of pH on color development. SF-2M Spectrophotometer; l = 2 cm; [Ga] = [formaine] = $= 2.2 \times 10^{-5}$ M; λ = 634 mμ.

The absorption band of formazine itself also shifts with changes in the pH; this is related to the existence of different ionic forms of formazine which develop in solution with changes in the acidity. At pH < 4 formazine only dissociated through its sulfo sulfonate groups, and only one type of ions is present in solution, the absorption curves at pH 2, 3, and 4 (Fig. 1) have the maximum in the same position. At pH > 4 dissociation of formazine through its phenolic hydroxyl groups becomes possible, and new types of ions are formed in solution; as a result of this, in the given pH range, there is observed a shift in the absorption curves of formazine to the long wavelength side of the spectrum.

Within the pH range 2-5, formazine hardly absorbs light at all at 634 mμ, i.e., at the wavelength at which maximum absorption is observed in the case of its compound with gallium. Accordingly, this region of the spectrum is the most suitable for the photometric determination of gallium.

TABLE 2

Effect of Temperature on the Rate at which the Optical Density Becomes Constant

Temperature, °C	Time for equilibrium to be established, hr	Optical density of solutions cooled to 20°
85–90	0,5	0,568
70—75	1	0,566
65—60	2	0,570
50–45	6	0,568
30–40	10	0,566
18–20	20—34	0,566

The molar ratios which obtain during the interaction of gallium with formazine were established by the "continuous change" method [5] at pH 3 and 6. The original solutions of gallium salt and formazine had a concentration of 5.0×10^{-6} M. The mixtures were kept at 60° for two hours and then at room temperature for one hour. The optical density was measured at 634 mμ. At the same time the optical density of solutions of formazine of the same concentration was measured. The experimental results are shown graphically in Fig. 2, in which the optical densities of the mixtures, corrected for the absorption of formazine, are plotted along the ordinate. As is evident from Fig. 2, maximum absorption of the solutions, both at pH 3 and at pH 6, is observed when 1 mole of formazine corresponds to 1 g. atom of gallium. Thus, the composition of the gallium compound formed does not depend on the acidity of the medium, and the shift of the absorption curve at pH 6 (Fig. 1) can only be the result of a change

TABLE 3

Optical Density of Solutions with Variable Concentrations of Gallium Ions

Molar ratio Ga : R*	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D	Molar ratio Ga : R	D
1 : 1	0,568	2 : 1	0,575	5 : 1	0,606	10 : 1	0,628	20 : 1	0,635
1 : 1	0,563	2 : 1	0,594	5 : 1	0,606	10 : 1	0,633	20 : 1	0,625
1 : 1	0,568	2 : 1	0,586	5 : 1	0,594	10 : 1	0,625	20 : 1	0,630
Mean $D_{equilib}$	0,566		0,585		0,602		0,629	D_{max}	0,630

*R – formazine molecule.

in the structure of the compound. It is highly probable that at this pH the coordinated ion is different from the dissociated form of formazine observed at pH 3.

The formation of a compound between gallium and formazine at another ratio differing from 1 : 1 is apparently possible, when excess complexing agent is used, as indicated by the asymmetric branch of the curve on the composition–property diagram (Fig. 2).

The results of a study of the effect of the pH on the optical density of solutions of the compound of gallium and formazine at a molar ratio of 1 : 1 are shown in Fig. 3. Prior to the measurements, the solutions were kept for two hours at 60° and then for an hour at 20°. The existence of maxima at pH 3 and 6 on the pH–optical density curve (Fig. 3) once again confirms the possibility of the formation of two different compounds of gallium, depending on the pH of the medium.

In our subsequent work gallium was determined photometrically at pH 3, since at this pH the reagent exhibits its highest sensitivity (Fig. 3), and also its highest selectivity (Table 4).

The rate at which the color develops is strongly dependent on temperature. While maximum light absorption is observed after only half an hour at 85-90°, at room temperature it is observed after 20 hr.

The effect of temperature on the rate at which equilibrium is established was studied using solutions containing gallium and formazine in a molar ratio of 1 : 1, at pH 3. The optical density of the solutions was measured at 20°. In experiments where heating was necessary, the solutions were cooled to 20° and kept for one hour at this temperature prior to optical density measurements. The color intensity of cooled solutions with a pH of 2-4 does not change for a long time; the color intensity of solutions with pH > 5 appreciably weakens with time. The relationship between the rate at which the reaction equilibrium is established and the temperature is shown in Table 2.

TABLE 4

Determination of Gallium with N,N' Di-2-hydroxy- 5-sulfophenyl)-C-cyanoformazine in the Presence of Zinc and Aluminum

Taken, μg	Found, μg	Error (relative), %	Taken, μg	Found, μg	Error (relative), %
Ga—1,40	1,40	0,00	Ga—1,40	1,40	0,00
Ga—1,40	1,40	0,00	Ga—1,40	1,40	0,0
Al—13 600			Zn—2 520	—	
Ga—1,40	1,38	1,81	Ga—1,40	1,40	0,0
Al—27 000	—		Zn—5 040	—	
Ga—1,40	1,44	+2,85	Ga—1,40	1,45	+2,90
Al—54 000			Zn—6 300	—	
Ga—1,40	1,50	+7,74			
Al—67 500	—				

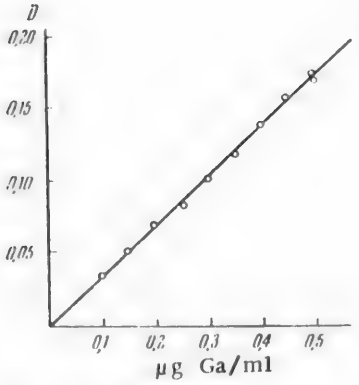


Fig. 4. Calibration curve for the determination of gallium. FÉK-M photocolorimeter; red filter; l = 1 cm.

The molar extinction coefficient was determined by the "saturation" method. The original concentration of the components was 1.25×10^{-5} M while the pH was 3.1. In order to suppress dissociation of the compound formed, excess gallium ions at the rate of 2 , 5 , 10 , and 20 times that stoichiometrically necessary were added. The solutions were kept for two hours at 60° and one hour at 20°.

The optical density was measured on a SF-2M spectrophotometer at 634 mμ in a cuvette with a layer thickness of 2 cm; water was used as the reference solution. As is evident from the results given in Table 3, dissociation of the complex is suppressed when there is only a tenfold excess of Ga^{3+} ions in solution. The value of molar extinction coefficient ε calculated from the mean value D_{max} is 25.200; this indicates that the reagent has a fairly high sensitivity.

The values of the optical density of solutions in which the dissociation of the complex compound has been suppressed, and of solutions with an equilibrium concentration, and which are shown in Table 3, were used for calculating the dissociation constant of the compound of gallium with formazine [6]: $K_{dissoc.} = \frac{\alpha^2}{1-\alpha} \cdot C$, where $\alpha = \frac{D_{max} - D_{equilib.}}{D_{max}}$ and C is the original concentration of the components in solution, equal to 1.25×10^{-5} M. The approximate value of the dissociation constant was found to be $K = 1.45 \times 10^{-7}$.

Aqueous solutions of the compound of gallium with formazine do not opalesce in ultraviolet light, and conform the Beer's law up to gallium concentrations of 2.5 μg/ml. Under the conditions established (pH 3, 634 mμ) the minimum gallium concentration which can be determined is 0.05 μg/ml (for a layer thickness of 1 cm).

The compound is not extracted by ether, butyl and isoamyl alcohols, ethyl and amyl acetate, methyl ethyl ketone, hexanone, carbon tetrachloride, or benzene; it is readily soluble in water and alcohol.

Copper, nickel, cobalt, titanium, vanadium, and iron interfere with the photometric determination of gallium with formazine. At the same time, aluminum and zinc do not form colored compounds with formazine, and, accordingly, do not interfere with the determination of gallium.

The results obtained (Table 4) show that the reagent permits determination of down to 0.002% of gallium in aluminum, and down to 0.02% in zinc.

Determination of small amounts of gallium in aluminum.* An aliquot of aluminum metal (0.05-0.10 g) is dissolved in hydrochloric acid (1 : 1) by heating on a water bath, and the solution evaporated to a small volume (but not to dryness). The sirupy mass is washed into a graduated cylinder with an amount of 1 M sodium acetate such that the total volume of the liquid in the cylinder is 15 ml. By adding the appropriate amount of 1 M hydrochloric acid and 1 M sodium acetate solution, the requisite acidity is established (pH 3), using a glass electrode. The volume of the solution is adjusted to 20 ml with a solution of an acetate-hydrochloric buffer solution with a pH of 3 (50 ml of 1 M CH_3COONa and 48.5 ml of 1 M HC), 1.5 ml of a 0.5% aqueous solution of formazine is added, and the solution left overnight at room temperature. The optical density is measured at 634 mμ on a SF-2M or FÉK-M spectrophotometer with a red filter, relative to the same solution free from gallium; the layer thickness is 2 cm. The gallium concentration is determined from a calibration curve. The latter is constructed by measuring the optical density of acetate-hydrochloric acid solutions (pH 3) containing from 0.1 to 1.5 ml of 0.0001 M $GaCl_3$ solution in 20 ml (at 0.1 ml intervals), 2 ml of 1 M $AlCl_3$ solution free from gallium,** and 1.5 ml of a 0.5% solution of formazine.

SUMMARY

A description is given of the synthesis of N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine.

The possibility has been demonstrated of using N,N' di-(2-hydroxy-5-sulfopheny)-C-cyanoformazine for the photometric determination of gallium. At pH 3 the absorption band of the compound (634 mμ) is far removed from the absorption band of formazine (470 mμ); the molar extinction coefficient at pH 3 and 634 mμ is 25,200. Solutions of the compound conform to Beer's law within the range 0.050-2.5 μg Ga/ml.

It has been shown that N,N'-di-(2-hydroxy-5-sulfophenyl)-C-cyanoformazine permits the determination of gallium in aluminum and zinc at a ratio of Ga : Al = 1 : 50,000 and Ga : Zn = 1 : 5,000.

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*When aluminum contains impurities which interfere with the determination of gallium, such as copper or iron, it is necessary to remove the gallium, e.g., by extracting it with ether from hydrochloric acid solutions [7].

**Aluminum chloride is purified from gallium by precipitating the latter with cupferron from weakly acid solutions together with iron [8].

***Original Russian pagination. See C. B. translation.

A FLOTATION METHOD FOR STUDYING THE EFFECT OF RUBIDIUM PRESENT AS AN IMPURITY ON THE DENSITY OF KCl CRYSTALS, AND THE DETERMINATION OF THE RUBIDIUM CONTENT OF POTASSIUM SALTS

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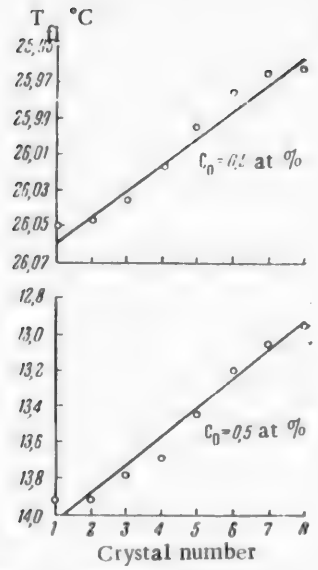
The flotation method of analysis is based on a comparison of the densities of two crystalline samples by measuring the flotation temperature (neutral equilibrium temperature) of the crystals in an indifferent liquid. The flotation method has been successfully used for analyzing the isotopic composition of several chemical elements, and enables a high accuracy to be achieved with simple equipment. Since the impurities present in crystals affect their density, the flotation method can be successfully applied to the study of the effect of impurities on the crystal density. The change in the density of the crystals from the true value can, in some instances, enable one to determine the concentration of the impurity in the original material and in crystals obtained from this material; it is possible to assess the changes in the crystalline lattice, and whether or not the impurity is isomorphous with the main component of the crystal. When, during the growth of the crystals, the impurity passes from the mother liquid into the crystals so that there is a change in the original concentration, the flotation method permits determination of the partition coefficient (distribution) of the main component and the impurity.

The present article is devoted to a description of the application of the flotation method for the determination of rubidium present as an impurity in potassium salts, and for the study of the effect of rubidium on the density of KCl.

The technique of the flotation method has been considered earlier [1].

Determination of the partition coefficient of potassium and rubidium during crystallization of a KCl melt containing rubidium as impurity. a) Purification of KCl and RbCl from impurities. In order to determine the partition coefficient it was necessary to have a KCl salt with a total concentration of impurity of $< 10^{-3}$ at.%, and to have a RbCl with a content of impurity < 0.1 at%. It was established spectrographically that potassium salts (KCl, KNO_3), chemically pure and analytical grade reagents produced by the Russian chemical industry, contain about 10^{-3} at.% rubidium. In order to cut down the rubidium content as well as the content of other elements in the potassium salts, KCl (chemically pure) was recrystallized five times from an aqueous solution, 25% of the crystalline phase being chosen in each operation. According to Hutchinson [2] purification of KCl by recrystallization ensures preparation of a salt with the requisite purity. Feit and Kubierzhskii [3] found that after 30 recrystallizations of carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$) the mother liquor is enriched with rubidium from 0.02 to 9.5 at%.

In order to establish the extent of purification of KCl from rubidium, an experiment was carried out in which 12 successive crystallization operations were made by cooling a saturated solution at 60° to 20°. After each recrystallization 73-75% of the KCl remained in the mother liquor. The crystalline phase was rejected. In the original salt the rubidium concentration was $C_0 = 0.001$ at%, while in the final solution (after 12 recrystallizations) it increased



The relation between T_{fl} of contaminated crystals as a function of the series number of the crystal during extraction from the salt melt.

to C" = 0.01 at.%. The partition coefficient α was determined from the relation (see [4]):

$$\alpha^n = C''/C_0$$

where n is the number of the degree of separation, corresponding to 12 crystallization operations, in which 73-75% of material from the mother liquor was taken. Calculation gives (see [4]) for this factor the value n = 3.6. From which we find that: α is about 1.9. Since, during the purification, it was necessary to remove rubidium from KCl, the mother liquor after each precipitation was rejected. In the range 60° to 20° about 25% of the salt crystallized out; this corresponds to a degree of separation of about 0.7. From the preceding calculations it is evident that in order to change the rubidium concentration ten times, a degree of separation of 3.6 is required. Since one crystallization operation corresponds to a degree of separation of 0.7, five operations should be sufficient for preparing KCl crystals containing about 10^{-4} at.% rubidium. In this way 10 g of KCl was prepared which contained less than 10^{-3} at.% of Na and Ca and about 10^{-4} at.% Rb according to spectrographic analysis.

RbCl was purified from impurities by the ionic mobility technique according to a technique described earlier [5].

b) Experimental procedure. In order to determine the partition coefficient α for potassium and rubidium during crystallization of a chloride melt, five samples of KCl freed from impurities were prepared. RbCl was added to four of these samples in such an amount that its concentration in the samples was as follows:

Sample No. 1 C_0 = 5.0 at. %
Sample No. 2 C_0 = 0.5 at. %
Sample No. 3 C_0 = 0.05 at. %
Sample No. 4 C_0 = 0.005 at. %
Sample No. 5 C_0 = 0.000 at. %

From each sample 5-8 crystals with a weight of q = 12-14 mg were prepared by a method described in [1]. The crystals were grown from salts fused at 780° in a platinum crucible. The original amount of salt Q in the crucible was determined by weighing. The crystals from each sample containing rubidium were floated together with crystals from sample No. 5. The flotation temperature T_{fl} of the pure crystals was compared with T_{fl} of a quartz float; this made it possible to assess the reproducibility of the density of pure crystals from one experiment to the other. Crystals from samples Nos. 1-4 were grown as equal in size as possible. Marks were made on some of them (see [1]) in accordance with the series number of the crystal during their growth.

It follows from Table 1 that the rubidium present as impurity appreciably depresses T_{fl} of the crystals as compared with T_{fl} of pure crystals. Accordingly, the density of KCl increases with increasing RbCl concentration. At a concentration of C_0 = 0.005-0.05 at.%, the density of the contaminated crystals is independent of the number of the crystal in individual experiments (see Expts. Nos. 1-4). For C_0 = 0.5-5.0 at.%, T_{fl} of the contaminated crystals is already dependent on the series number of the crystal (see Expts. Nos. 5-6); it decreases with the increase in the series number of the crystal. It is clear from column 7, Table 1, that the reproducibility of T_{fl} of the pure crystals relative to the float is fairly good. In Expts. 5 and 6, the crystals were floated in 1,3-dibromopropane to which ethylene bromide had been added; accordingly the values of the differences in the flotation temperatures of the pure crystals and float are different to those in Expts. Nos. 1-4. In column 8, the difference ΔT between crystals from pure KCl and from contaminated crystals is calculated for Expts. 5 and 6, using only T_{fl} for the crystals corresponding to the first two series numbers. T_{fl} was determined by means of a Beckmann thermometer, the scale of which was accurate to ± 0.1°C.

In the diagram is shown a curve relating T_{fl} of crystals in Expts. 5 and 6 to the series number of the crystal. The difference between the flotation temperatures of two adjacent crystals, $\Delta t = \left[\frac{\text{degree C}}{\text{1 crystal}}\right]$, necessary for the calculations, is determined from the slope of the straight lines.

TABLE 1

Expt. No.	C_0, at.%	Q.mg	Crystal number	T_{fl} of contaminated crystals, °C	T_{fl} of pure crystals, °C	ΔT_{f-p} (float - pure crystals)	ΔT (pure crystals and contaminated crystals)
1	0,005	360	1	13,278	13,293	0,323	0,015
			2	13,278	13,293		
			3	13,278	13,293		
			4	13,280	13,294		
			5	13,275	13,291		
2	0,005	360	1	13,283	13,296	0,323	0,016
			2	13,283	13,296		
			3	13,283	13,300		
			4	13,282	13,302		
			5	13,285	13,303		
3	0,05	360	1	13,129	13,293	0,323	0,163
			2	13,129	13,293		
			3	13,129	13,293		
			4	13,129	13,294		
			5	13,132	13,291		
4	0,05	360	1	13,133	13,296	0,323	0,164
			2	13,134	13,296		
			3	13,136	13,300		
			4	13,137	13,302		
			5	13,136	13,303		
5	0,5	360	1	26,050	27,483	—1,362	1,434
			2	26,047	14,483		
			3	26,035	27,483		
			4	26,017	27,482		
			5	25,995			
			6	25,975			
			7	25,965			
			8	25,961			
6	5,0	300	1	13,905	27,483	- 1,362	13,585
			2	13,890	27,483		
			3	13,788	27,483		
			4	13,695	27,482		
			5	13,427			
			6	13,201			
			7	13,072			
			8	12,942			

TABLE 2

C_0	0,005	0,05	0,5	5,0
ΔT, °C	0,016∓0,002	0,164∓0,002	1,435∓0,005	13,585∓0,100
$\Delta T_{true} = \Delta T\left(1-\frac{\beta_k}{\beta_{liq.}}\right)$	0,014∓0,002	0,143∓0,002	1,260∓0,005	11,9∓0,1
$K=\frac{\Delta T_{true}}{C_0}$	2,7∓0,4	2,86∓0,04	2,52∓0,01	2,38∓0,02

In Table 2 are given the mean values of ΔT, taken from Table 1, and the values of ΔT_{true} calculated from ΔT taking into account the thermal expansion of the flotation liquid and the crystals.

Assuming that RbCl present as an impurity in KCl up to a concentration of 5 at.% and addition of ethylene bromide to 1,3-dibromopropane insignificantly affect the thermal expansion coefficient of the KCl crystals and of the flotation liquid, in subsequent calculations the thermal expansion coefficient of 1,3-dibromopropane:

and the thermal expansion coefficient of KCl were used:

$$\beta_{\text{liquid}} = 902 \cdot 10^{-6} \frac{1}{\text{deg C}} \qquad [1]$$

c) Determination of partition coefficient. As a result of measurements and preliminary calculations the values of the following factors were obtained: Q, q, C_0, Δt, ΔT. On the basis of these results it is possible to calculate the partition coefficient of potassium and rubidium which determines the extent to which the rubidium passes from the salt melt into the crystals.

Let us denote the RbCl concentration in the crystal grown by C'_n, where n is the series number of the crystal, while the concentration of RbCl in the fused salt immediately after the growth of the given crystal is denoted by C''_n. When $q \leq Q$ (this is true for the experiments given in Table 1), it can be assumed approximately that the rubidium concentration in the first two crystals differs insignificantly, while the concentration of rubidium in the fused salt after removing these crystals:

$$C''_1 \simeq C''_2 \simeq C_0. \qquad (1)$$

Since the relative rubidium content in KCl is low, the partition coefficient can be written as the ratio of the rubidium concentration in the crystal and in the fused salt:

$$\alpha = C'/C''. \qquad (2)$$

For the first two crystals, according to [1],

$$\alpha = C'_1/C_0. \qquad (3)$$

Rayleigh's relation (see, e.g., [4]), which relates the partition coefficient to the concentration and amount of material in the residual fused salt, can be written as:

$$C''_n = C_0 \left(\frac{Q''_n}{Q}\right)^{\varepsilon}, \qquad (4)$$

where $\varepsilon = \alpha - 1$, $Q''_n = Q - nq$. From (2) and (4) we find that

$$C'_n = \alpha C_0 \left(\frac{Q - nq}{Q}\right)^{\varepsilon}.$$

From which

$$C'_{n+1} - C'_n = \alpha C_0 \left[\left(\frac{Q - (n+1)q}{Q}\right)^{\varepsilon} - \left(\frac{Q - nq}{Q}\right)^{\varepsilon}\right]. \qquad (5)$$

In contrast to $K = \frac{\Delta T_{\text{true}}}{C_0}$ (see Table 2) the ratio of ΔT_{true} to the RbCl concentration in the first crystal gives the true proportionality coefficient, i.e.

$$K_{\text{true}} = \frac{\Delta T_{\text{true}}}{C'_1}. \qquad (6)$$

Or, using (3), we have:

$$K_{\text{true}} = \frac{\Delta T_{\text{true}}}{\alpha \cdot C_0}. \qquad (6a)$$

From this, the difference between the concentrations of the first and second crystals will be:

$$C'_2 - C'_1 = \frac{-\Delta t_{\text{true}}}{K_{\text{true}}} = \frac{-\Delta t_{\text{true}}}{\Delta T_{\text{true}}} \alpha C_0, \qquad (7)$$

where

$$\Delta t_{true} = \Delta t \left(1 - \frac{\beta_k}{\beta_{liquid}}\right).$$

Equating (5) and (7), we have:

$$\frac{\Delta t_{true}}{\Delta T_{true}} = \frac{\Delta t}{\Delta T} = \left(\frac{Q-q}{Q}\right)^{\varepsilon} - \left(\frac{Q-2q}{Q}\right)^{\varepsilon}. \tag{8}$$

The first part of expression (8) can be resolved into a McLauren's series in the ε'th degree, by confining it to the first member of the resolution (the second member only introduces a negligible correction). After transformation, we have:

$$\frac{\Delta t}{\Delta T} = \varepsilon \ln \frac{Q-2q}{Q-q}. \tag{9}$$

Using equation (9), it is easy to calculate the partition coefficient $\alpha = 1 + \varepsilon$ for Expts. 5 and 6.

For Expt. 5: $C_0 = 0.5$ at.%, $\Delta t = 0.015 \frac{\text{deg C}}{\text{crystal}}$, $\Delta T = 1.434°$

$Q = 360$ mg, $q = 14.5$ mg.

From which $\alpha = 0.76$.

For Expt. 6: $C_0 = 5.0$ at.%, $\Delta t = 0.158 \frac{\text{deg C}}{\text{crystal}}$, $\Delta T = 13.58°$

$Q = 300$ mg, $q = 12.5$ mg.

From which $\alpha = 0.74$.

From the calculated values of α it follows that rubidium enters the crystal phase of the KCl, increasing thereby its concentration by $1/\alpha$ for one separation step.

The accuracy with which α is determined depends mainly on the accuracy with which the crystals are weighed, and on the accuracy of the determination of Δt. In our previous calculations the mean value of Δt was calculated for eight crystals, i.e., it was assumed that the flotation temperatures of the crystals changes linearly with the increase in the series number of the crystal. In actual fact, as is evident from Eq. (9), the value of Δt increases with the increase in the crystal number (see Fig. 1). It follows from this that a more accurate value of α can be obtained by determining the slope of the tangent and the curve at the origin. In the previous experiments, as is evident from the curve (Fig. 1), this could not be done because of the scatter in the values of T_{fl}. This scatter can be explained by the fact that the size of the crystals is not constant enough. An assessment carried out on the basis of Eq. (9) shows that a mean value of Δt obtained on the basis of eight crystals of equal size ($q = 10$ mg, $Q = 400$ mg) will be greater than Δt for the first two crystals by 10-15%.

There is still another possible source of error, which is related to insufficient mixing of the molten salt during the growth of the crystal. When the melt is not adequately stirred it is necessary to grow crystals at the minimum growth rate.

Effect of RbCl on the density of KCl crystals. The values of ΔT_{true} characterize the changes in density as a function of rubidium concentration. Let us assume that for a value of $C_0 \leq 5$ at.%, the coefficient K_{true}, which depends on the packing of the rubidium ions in the KCl lattice, remains constant, i.e., that the packing coefficient is independent of the concentration, within the limits indicated. For Expts. 5 and 6 it is possible to calculate by means of Eq. (6a) that the value of $K_{true} = 3.3 \pm 0.4$. In Table 2 are given the values $K = \alpha \cdot K_{true}$, which increase with decreasing concentration C_0. Taking $K_{true} = 3.3$ to be constant, it is possible to calculate the values of α for Expts. 1-4 and to find C' by means of (3). The corresponding values are given in Table 3.

If the density of pure KCl crystals is denoted by ρ_0, while the density of contaminated crystals is denoted by ρ', it is possible to write:

$$\rho' - \rho_0 = \Delta\rho = \rho_0 (\beta_{liquid} - \beta_k) \Delta T, \tag{10}$$

TABLE 3

C_0, at. %	α	C', at. %
5,0	0,74	3,7
0,5	0,76	0,38
0,05	0,88	0,044
0,005	0,8–0,9	0,004–0,005

TABLE 4

C', at. %	3,7	0,38	0,044	0,004
γ	0,00578	0,00596	0,00585	0,0058

where ΔT is the difference in the flotation temperatures of these crystals. At the same time we have:

$$\Delta\rho = \gamma \cdot C', \tag{11}$$

where γ is a constant coefficient.

From (10) and (11) we find

$$\gamma = \frac{\rho_0 (\beta_{\text{liquid}} - \beta_1)\ \Delta T}{C'} \tag{12}$$

where $\rho_0 = 1.988\ \text{g/cm}^3$. By means of (12) and using the results from Tables 2 and 3, the values of γ for various concentrations are calculated.

It follows from Table 4 that γ = const. From which relation (11) is linear, i.e.

$$\Delta\rho = 0.6 \cdot 10^{-2} C'\ \text{g/cm}^3,$$

where C' is in at.%.

It is interesting to note that Pick and Weber have also established a linear relation between the density of KCl and the concentration of $CaCl_2$ present as an impurity [6].

$$\Delta\rho = -0.8 \cdot 10^{-2} C'\ \text{g/cm}^3,$$

where C' is the concentration in at.%, the maximum value of which in these experiments was 2×10^{-2} at.%.

Knowing the experimental value $K_{\text{true}} = \Delta T / C'_1 = 3.3$, it was interesting to compare it with the corresponding coefficient calculated on the assumption of the independence of the packing of the Rb^+ ions on the concentration in the KCl crystal lattice. Let us denote the calculated coefficient by K_{calc}. Further, let the flotation temperature of pure crystals be denoted by T_0, while that of crystals contaminated with rubidium be T_1. For the given values of T_0 and T_1 the densities of the crystals coincide with the density of the flotation liquid; accordingly it is possible to write:

$$\rho_0 = \frac{\mu_0}{V_0 (1 + \beta_k \cdot T_0)} = \rho_{\text{liquid}} (1 - \beta_{\text{liquid}} \cdot T_0), \tag{13}$$

where μ_0 is the molecular weight of KCl, V_0 is the molecular volume of KCl at 20°, ρ_{liquid} is the density of the flotation liquid at 20°, and ρ_0 is the density of pure KCl crystals.

$$\rho_1 = \frac{\mu_0 (1 - C') + \mu_1 C'}{[V_0 (1 - C') + V_1 \cdot C'] (1 + \beta_k T_1)} = \rho_{\text{liquid}} (1 - \beta_{\text{liquid}} \cdot T_1), \tag{14}$$

where μ_1 is the molecular weight of RbCl, V_1 is the molecular volume of RbCl in the KCl crystals, and $100 \cdot C'$ is the RbCl concentration in at.%.

Subtracting Eq. (13) from (14) we find:

$$\Delta T = T_0 - T_1 = \frac{\left(\frac{\mu_0}{V_0} - \frac{\mu_1}{V_1}\right) V_1 \cdot C'}{\rho_{\text{liquid}} (\beta_k - \beta_{\text{liquid}}) \cdot V_0}\ 10^{-2}. \tag{15}$$

From which:

$$K_{calc.} = \frac{\Delta T}{C'} = \frac{\frac{V_1}{V_0}\left(\frac{\mu_1}{V_1} - \frac{\mu_0}{V_0}\right)}{\rho_{liquid}(\beta_{liquid} - \beta_k)} 10^{-2} \qquad (16)$$

Equating $K_{calc.} = K_{true} = 3.3$, and substituting in (16) the known values of $\rho_{liquid} = 1.985$ g/cm^3, $\rho_0 = 1.988$ = 1.988 g/cm^3, and $V_0 = 37.45$ cm^3/ mole, it is possible to calculate the molecular volume of RbCl which can be assigned to it in the KCl crystal, if, thereby, the molecular volume of KCl does not change. Calculations based on (16) give for V_1 a value of 51 ± 1 cm^3/mole; at the same time it is known that the molecular volume of RbCl is equal to 43.2 cm^3/mole.

Accordingly, the presence of rubidium ions in the crystal lattice of KCl leads to a deformation of the lattice, the size of the latter being increased. Under these conditions the expansion of the crystal lattice is relatively small, since the density of the contaminated crystal also continuously increases with increasing RbCl concentration.

Determination of the rubidium concentration in potassium by the flotation method. The sensitivity of the flotation method for a certain impurity concentration will be very high. In fact, it is clear from Table 2 that a change of 0.001 at.% of rubidium in KCl crystals leads to a change in T_{fl} of 0.003°, which corresponds to a change of about 3 γ in the density of KCl. In general, the flotation method is applicable to the quantitative analysis of any two chemical compounds which form between them solid solutions in the concentration range we are interested in. The flotation method includes the following operations:

Preparation of standard samples with a known relative content of both chemical compounds; growth of crystals from the standard samples; the choice of a flotation liquid which is chemically neutral to the crystals and similar to them in density; determination of the thermal expansion coefficient of the liquid and the crystals (a very simple and accurate flotation method has been developed for crystals [7]). Further, by floating the crystals, the relation between T_{fl} of the crystals and the concentration of the components is established, and a calibration curve is constructed.

Determination of the relative contents of the two components in the test material. For this purpose the material should be purified from foreign impurities to the same condition as the standard samples. Crystals are then prepared and their T_{fl} determined relative to that of the standard crystals (or with respect to quartz floats). The concentration of both components is finally found from the calibration curve.

Let us consider the technique for the determination of the rubidium concentration of rubidium in potassium. The curve relating the flotation temperature of contaminated crystals ΔT and the rubidium concentration in the crystals – C' – is found from (6) and from Table 2, i.e.

$$C' = \frac{\Delta T}{K_{true}}\left(1 - \frac{\beta_k}{\beta_{liquid}}\right) \qquad (17)$$

When 1,3-dibromopropane is used as the flotation liquid, Eq. (17) is written:

$$C' \text{ (at.\%)} = 0.27 \cdot \Delta T \text{ (deg C)}$$

A mixture of ethylene bromide and chlorobenzene can also be used as a flotation liquid. The thermal expansion coefficient of this mixture can be calculated with reasonable accuracy from the known thermal expansion coefficients of ethylene bromide and chlorobenzene, on the basis that these values are additive.

At a certain rubidium concentration of the original salt, it is necessary to take into account the partial separation of rubidium and potassium which during the growth of crystals from a molten salt, i.e.

$$C_0 = \frac{C'}{\alpha} = \frac{\Delta T}{K}\left(1 - \frac{\beta_k}{\beta_{liquid}}\right) \qquad (18)$$

In Table 2 are given the values of K found for different rubidium concentrations. The content of other impurities amounted to $< 10^{-3}$ at.%. Naturally, the values of K can only be used in the analysis in those cases where the content of the other impurities is also $\leq 10^{-3}$ at.%. When this condition is fulfilled the accuracy with which

the rubidium concentration in potassium can be determined will only depend on the accuracy with which ΔT can be read, and on the value of K (see Eq. (18)].

Using (18), on the basis of the results given in Table 2 we find that in the range 0 to 5 at.%, the absolute error in the determination C_0 amounts to $\pm$ (1-2) 10^{-3} at.%, independently of C_0. As experiments have shown, the presence of other impurities in the test salt in amounts of about 10^{-2}% correspondingly increases the error in C_0 to about 10^{-2} at.%.

Foreign impurities can be removed by the method of ionic mobilities described in [5]. When this purification method is used, rubidium, which has almost the same ionic mobility as potassium, is not removed from the salt, while the remaining impurities (cations and anions, apart from the chloride ion) are readily removed. The only exception is cesium, whose ionic mobility is also close to that of potassium. Cesium is, however, usually present as a microcomponent, and it can be ignored.

Thus, if the relationship $\Delta T(C_0)$ is known, the determination of the rubidium concentration of potassium consists of the following successive operations:

Purification of the test material from foreign impurities to the required condition. The final product is prepared in the form of the chloride, the amount necessary being about 300 mg.

Growing 4-6 crystals of KCl from the molten salt (see [1]).

Determining the flotation temperature of these crystals relative to T_{fl} of standard crystals or relative to T_{fl} of a quartz float graduated against standard crystals. And, finally, determination of the rubidium concentration C_0 from a calibration curve or from Eq. (18).

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SUMMARY

The partition coefficients of rubidium between molten KCl and the crystalline phase at about 780° for RbCl contents of 5.0 to 0.005 at.% in KCl have been determined by a flotation method. It has been shown that the partition coefficient α varies from 0.74 to 0.9, i.e., at low RbCl concentrations the transfer of rubidium into the crystalline phase occurs with less partitioning than at high concentrations.

The density of KCl crystals increases with increasing rubidium concentration according to the equation: $\Delta = 0.6 \times 10^{-2} \cdot C'$.

RbCl molecules present in KCl crystals increase the size of the crystal lattice to a greater extent than would be possible if the RbCl molecules were found in the KCl lattice with a characteristic molecular volume.

It has been shown that the flotation method can be used for the determination of rubidium concentration in potassium salts with an accuracy of up to (1-2) 10^{-3} at.%.

An assessment is made of the partition coefficient of rubidium and potassium during the crystallization of their chlorides from an aqueous solution (α = 1.9). During this process, as is known, the rubidium concentrates in the solution.

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FLAME PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF CESIUM IN NATURAL SAMPLES ENRICHED WITH POTASSIUM

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The presence of potassium as an impurity in solution increases the radiation intensity of rubidium in the flame [1-3]. This fact has been used for increasing the sensitivity of the flame photometric method of determining Cs in minerals [4]. This technique specifies the addition of 2500 μg of potassium/ml to the solution; larger amounts are undesirable, since the characteristic K radiation creates a background around the cesium wavelength, thereby depressing the sensitivity of the method.

Determination of small amounts of cesium (ten thousandths of a percent) in natural materials is only possible with large amounts of sample (a minimum of 5 g/50 ml). The optimum potassium content in this case is 2.5-3.0%. In samples which are rich in potassium, it is impossible, by simply increasing the amount of the aliquot, to increase the sensitivity of cesium determination, since with increasing cesium concentration in the test solution, the potassium concentration increases to the same extent. Determination of small amounts of cesium in such samples can only be carried out after removing the excess potassium.

We have studied the possibility of separating microamounts of cesium from macroamounts of potassium by coprecipitating cesium with sparingly soluble ammonium silicomolybdate. Of the coprecipitants used hitherto [5-8] for cesium, only thallium chloroplatinate can be used for separating it from potassium [8]. For analytical purposes, however, thallium chloroplatinate is not very suitable, since it only permits removal of not more than 80% of the cesium present in solution.

Silicomolybdic acid is one of the best precipitants for cesium. The sensitivity of this reaction, according to Moser and Ritschel [9], is 1.58×10^{-4} g/ml. The potassium salts of this acid are readily soluble.

In developing conditions for coprecipitating gamma amounts of cesium with ammonium silicomolybdate, we made use of published results [10, 11] which indicate that the solubility of cesium silicomolybdate decreases with increasing acidity of the medium; the solubility of ammonium silicomolybdate itself sharply decreases when excess ammonium chloride is present in solution. By alternately changing these factors in the presence of sodium silicomolybdate and gamma amounts of cesium in solution, and by determining the extent to which Cs is entrained by the ammonium silicomolybdate precipitated, we found that in the case of a solution containing 0.1 g H_2SO_4/ml, 0.2 g NH_4Cl/ml, and 1.4 g $2Na_2O \cdot SiO_2 \cdot 12MoO_3$/ml, cesium is completely (95-100%) entrained by the ammonium silicomolybdate which is precipitated under these conditions (Table 1).

Subsequently, we checked on the degree to which cesium is coprecipitated with ammonium silicomolybdate under the optimum conditions, in the presence of potassium. Up to 20,000 μg K/ml was added to the solution (corresponding to 20% K on dissolving 5 g of it in 50 ml of solution). It was established that the extent to which cesium is entrained (95-100%) by the ammonium silicomolybdate is independent under these conditions of the presence of potassium in the solution. Most of the potassium (99.8%) remains in solution.

TABLE 1

Coprecipitation of Cesium with Ammonium Silicomolybdate from 50 ml of Solution Containing 0.1g H_2SO_4/ml, 0.2 g NH_4Cl/ml, and 1.4 g $2Na_2O \cdot SiO_2 \cdot 12MoO_3$/ml

Amount taken for coprecipitation, μg/ml	Cs found in the precipitate dissolved in 50 ml of an ammoniacal solution, μg/ml						Cs coprecipitated, %
	expt. no.					mean	
	1	2	3	4	5		
0,2	0,19	0,2	0,17	0,21	0,20	0,19	95,0
1,0	1,0	1,1	0,9	1,0	1,0	1,0	100,0
10	10	9,9	9,8	10,2	10,1	10,0	100,0
20	19,8	20,00	20,10	19,90	20,00	19,96	99,8

TABLE 2

Control Determinations of Cesium

Sample	Potassium content of the sample, %	Cs found in the sample, %	Cs added, %	Cs found after addition, %	Relative error, %
Pegmatoid granite	4.73	0.0007	0.0007	0.0015	+ 14.1
Parfiro granite	3.5	0.0006	0.0006	0.0011	− 16.6
Biotite parfiro granite	4.5	0.0011	0.0011	0.0022	0
Biotite medium grained granite	7.13	0.0002	0.0002	0.0004	0

The completeness of removal of microamounts of cesium during the analysis of various granite rocks, using 5 g samples, and with preliminary separation of the cesium from excessive amounts of potassium by means of ammonium silicomolybdate, was demonstrated by introducing additional amounts of Cs to samples containing some ten thousandths parts of a percent of Cs, and finding the amount of cesium introduced, by difference, by carrying out determinations before and after the addition (Table 2). The maximum losses did not exceed 16.6%. The limiting sensitivity with which Cs can be determined on a flame setup in the presence of 2500 μg potassium/ml is the same as in [7], viz, 0.1-0.2 μg/ml).

The chemical preparation of the samples is described below. The technique used for carrying out flame photometric measurements has been published earlier [4].

Experimental procedure. Preparation of silicomolybdic reagent: 1) To 100 ml of a 10% NaOH solution is added 38 g of MoO_3 in small portions (1-1.5 g) with stirring until complete solution is obtained. The solution is heated before addition of each portion of MoO_3. The solution obtained should be free of precipitate.

2) The sodium silicate solution is prepared from 1.5 g of $Si(OH)_4$, 2 g of NaOH, and 50 ml H_2O.

3) Twelve ml of H_2SO_4 (sp. gr. 1.84) is mixed with 100 ml H_2O.

Initially the molybdate and silicate solutions are poured together; the sulfuric acid solution is then added slowly in small portions to the mixture obtained. The reagent may be turbid; if this is the case, it should be filtered. The reagent is bright yellow in color. Mixing is carried out in the cold.

Sample preparation. A five g sample is decomposed with a mixture of hydrofluoric, sulfuric, and nitric acids (40-50 ml HF, 10 ml H_2SO_4, and 1 ml HNO_3) in a No. 8 platinum basin. To the dry residue obtained after treatment with the acid is added 5 ml of H_2SO_4 in order to remove HF completely, and the test again evaporated to the appearance of sulfuric acid fumes. After cooling, the residue is transferred by means of 50 ml H_2O into a 100 ml beaker and the precipitate filtered off; the latter is washed with hot water. The filtrate plus the wash

liquors are evaporated to a volume of 50 ml. Cesium is removed from the solution obtained at room temperature. For this purpose the solution is acidified with 3 ml H_2SO_4 (sp. gr. 1.83). After careful mixing, to the solution is added 15 ml of the silicomolybdic reagent, also with careful stirring, and, finally, to the solution obtained is added 10 g of dry, well ground NH_4Cl. During this stage the yellow precipitate of ammonium silicomolybdate separates out. After 20-30 min the precipitate is filtered through a filter ("white band"), the beaker and the precipitate are washed three times with a wash liquor which has the following composition: 500 ml H_2O, 30 ml H_2SO_4 (sp.gr. 1.84), and 100 ml NH_4Cl.

After washing, the precipitate plus filter are transferred to the same beaker and treated with 25-30 ml of ammonia solution (1 : 1), and the whole stirred until the ammonium silicomolybdate has completely decomposed; this is readily observable by the disappearance of the yellow precipitate. The filtrate is immediately filtered into a standard flask (50 ml). To it is added 5 ml of a K_2SO_4 solution containing 25,000 μg K/ml and the volume made up to the mark with water. Cesium is finally measured flame photometrically by means of the technique described previously [4]. A correction should, however, be made in this case, both for the standard and for the test solutions, by measuring the mean radiation which is detected by the apparatus on rotating the drum of the monochromator 7-10° on both the long wavelength and short wavelength side of the cesium line (852.1 mμ).

The standard reference solution is treated in exactly the same way as the solution of the sample. For this purpose, 50 ml of a Cs_2SO_4 solution is taken, whose cesium content is accurately known and is of the order of 1.5 μg Cs/ml. The solution is acidified with 3 ml of H_2SO_4, after which the cesium is coprecipitated as described above in the case of the test sample. The coprecipitation operations are carried out simultaneously for several samples and for one standard solution. A blank test is also necessary.

The suggested method, in which cesium is coprecipitated with ammonium silicomolybdate, can also be used for the flame photometric determination of small amounts of cesium in potassium salts.

SUMMARY

It has been established that cesium is coprecipitated from sulfuric acid solutions together with ammonium silicomolybdate.

A technique has been developed for the flame photometric determination of microamounts of cesium in natural materials with high potassium contents.

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DETERMINATION OF THE COPPER AND MANGANESE CONTENTS OF ORES BY NEUTRON RADIOACTIVATION ANALYSIS

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The content of copper, manganese, and other elements in various samples and aluminum alloys [1-7] has been determined by neutron activation analysis. A neutron stream of $10^{12}/cm^{-2}sec^{-1}$ from a nuclear reactor was used for activating the test samples. The work described here was carried out with the aim of establishing the possibility of using γ spectrometry in activation analysis, for the determination of the copper and manganese contents of rock samples, using a stream of activating neutrons with a low intensity (10^7-10^8 neutrons/$cm^{-2}sec^{-1}$). The use of a neutron stream of such an order is of the greatest interest for the determination of the content of the elements mentioned under drilling conditions. The copper ores from deposits are mainly inclusions of chalcopyrities ($CuFeS_2$) in enclosing rocks – syenites, diorites, syenite-diorites, quartz porphyries, granodiorite porphyries. The copper content in the test rocks varies from 0.03 to 0.9%, while that of manganese (MnO) varies from 0.01 to 0.3%.

The chemical composition of a syenite-diorite is given in Table 1. The method which we have developed for the quantitative determination of Cu and Mn is based on the phenomenon of the artificial radioactivity of elements which develop on radiating them with thermal neutrons, as a result of which nonradioactive (stable) elements become radioactive. All the same, not all the elements possess an equal capacity to be activated in a neutron stream. In addition, artificially radioactive elements, in decaying, possess different half-life periods and different types of radiation, while the particles and γ quanta emitted also have different energies.

In Table 1 are given the nuclear characteristics of the elements which compose the test ore. From these results it is clear that the natural copper isotope Cu^{63} has an effective activation cross section of 3.9 b, i.e., the copper isotope indicated is readily activated by thermal neutrons. The isotope is activated according to the reaction (n, γ): $Cu^{63} + {}_0n' \rightarrow Cu^{64} + \gamma$.

The radioactive isotope Cu^{64} decays with a half life period of 12.9 hr, emitting thereby β particles and γ quanta with an energy of 0.51 mev.

Manganese has an effective activation cross-section of 12.7 b, i.e., it is very readily activated by thermal neutrons. Activation proceeds according to the reaction $Mn^{55} + {}_0n' \rightarrow Mn^{56} + \gamma$.

The radioactive isotope Mn^{56} decays with a half life period of 2.6 hr, emitting thereby β particles and γ quanta with an energy of 0.84 mev.

On the basis of the data given above, the technique for the quantitative determination of Cu and Mn in ore samples reduced to the following: samples whose percentage contents of Cu and Mn were already known were taken, they were ground, and aliquots of the samples indicated, of a definite weight (120 g), were prepared; these were the so-called standard samples. These standards were then irradiated with slow neutrons from a Po-Be neutron source, whose activity was of the order of 20 C. A paraffin block was used to slow down fast neutrons.

TABLE 1

The Nuclear Characteristics of the Elements Present in Syenite-Diorite

Chemical composition of the sample	Percentage content	Effective activation cross-section, b	Percentage content of the isotope in the natural mixture	Radioactive isotope formed	Half-life period, $T_{1/2}$	Energy of the γ radiation, mev	Yield of γ-quanta per 100 decays, %	Calculated activity I in arbitrary units for an irradiation time of 72 hr
SiO_2	60 - 30	0,12	3,08	Si^{31}	2,7 hr	1,26	0,07	2160
TiO_2	0,8 –0,5	0,14	5,3	Ti^{51}	6 min	0,32	99,2	42
Al_2O_3	16—8,6	0,21	100	Al^{28}	2,3 min	1,78	100	42 000
Fe_2O_3	3,2							
FeO	3,2							
MnO	0,11—0,08	12,7	100	Mn^{56}	2,6 hr	0,84; 1,8; 2,1	99,7; 24,9; 14,8	11 430
MgO	2,2							
CaO	4—3	1,1	0,18	Ca^{49}	3.5 min	3,1; 4,05	90,10	77
Na_2O	3,5—2,6	0,54	100	Na^{24}	15 hr	1,368; 2,75; 3,86	100; 100; 0,05	20 000
K_2O	5,5—4,5	1,0	6,9	K^{42}	12,4 hr	1,51; 0,32	18,2; 0,2	2800
P_2O_5	0,3	0,23	100	P^{32}	14,3 days	—	—	—
Cu^{63}	0,5—0,35	3,9	69	Cu^{64}	12,9 hr	0,51	38	7000
	0,15	1,8	31	Cu^{66}	4,3 min	1,064	9	2700
Sr	0,001—0,001	1,3	9,8	Sr^{87}	2,7 hr	0,388	78	1
Ba	0,01—0,01	0,5	71,7	Ba^{139}	86 min	1,43; 0,63	19; 54,8	15
V	0,001—0,001	4,5	99,8	V^{52}	3,9 min	1,44	100	45

Fig. 1. Energy spectrum for the γ radiation of Cu^{64}.

Fig. 2. Energy spectrum for the γ radiation of Mn^{56}.

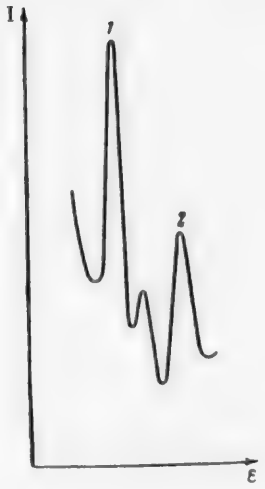

Fig. 3. Over-all energy spectrum for Cu (peak 1) and Mn (peak 2).

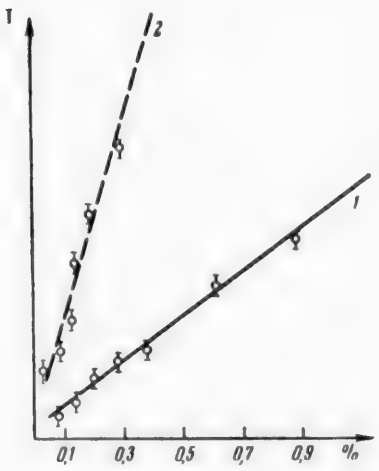

Fig. 4. Curve relating radiation intensity to Cu and Mn contents (for standard samples weighing 120 g). 1) For Cu; 2) for Mn.

The irradiation time was chosen so that a sufficiently high activity was obtained from the Cu^{64} isotope. In deciding on the irradiation time, the results of theoretical calculations of the expected activity of the various isotopes in the test sample were taken into account. Calculation of the activity of each isotope was carried out using the well-known formula [8]:

$$A = n \cdot \nu \cdot \sigma_{act.} N (1-e^{-\lambda}).$$

where $n\nu$ is the stream of thermal neutrons, σ_{act} is the effective activation cross section of the isotopes, N is the number of isotope atoms in the sample, λ is the decay constant equal to $(0.693\ t)/T\ (^1/_2)$, and $\underline{t}$ is the irradiation time.

On the basis of the theoretical results for the activity of the various isotopes, and on the basis of the half life periods, decay curves were constructed for each isotope in order to choose the optimum measurement conditions (the time from completion of activation to the beginning of the measurements was equal to 30 min).

The γ activity of the activated samples was measured by means of a scintillation γ spectrometer [9]. The technique of measuring reduced to recording the spectra of the γ radiation of the activated sample. In Fig. 1 is shown the energy spectrum of the Cu^{64} γ radiation recorded by means of the apparatus [on this there is clearly visible a radiation maximum ("peak") corresponding to an energy of 0.51 mev for the isotope], while in Fig. 2 is shown the energy spectrum of Mn^{56} actually recorded (this has a radiation maximum with an energy of 0.84 mev).

When both Cu and Mn were simultaneously present in the sample the spectrum shown in Fig. 3 was obtained, in which peak 1 corresponds to an energy of 0.51 mev for the Cu^{64} isotope, while peak 2 corresponds to an energy of 0.84 mev for the Mn^{56} isotope. Since the peak height is proportional to the concentration of the element in the sample, this enables one to assess the concentrations of the test elements in the sample. The isotopes were identified by measuring the decrease in the intensity of the peaks on the spectra with time, in order to determine their half life period.

TABLE 2

Determination of Copper and Manganese by Chemical and Radioactivation Methods

Sample No.	Rock	Found, %			
		Copper		Manganese	
		by the radioactivation method	by the chemical method	by the radioactivation method	by the chemical method
1	Syenite	0.03	0.05	0.14	0.16
2	Quartz porphyry	0.37	0.34	0.21	0.18
3	" "	0.41	0.35	0.08	0.09
4	Syenite-diorite	0.80	0.83	0.052	0.049
5	" "	0.21	0.17	0.13	0.15
6	Granodiorite-porphyry	0.68	0.65	0.04	0.05
7	Syenite-diorite	0.64	0.64	0.06	0.03
8	" "	0.15	0.18	0.08	0.09
9	Diorite	0.07	0.09	0.11	0.13
10	"	0.28	0.31	0.16	0.14
11	Syenite-diorite	0.79	0.89	0.028	0.024
12	Diorite	0.2	0.03	0.18	0.17

In order to determine Cu and Mn quantitatively in samples, on the basis of measurements of the γ spectra of standard samples, the curve shown in Fig. 4 was constructed. Such a curve was used for determining the Cu and Mn contents of samples with unknown contents of Cu and Mn. A large number of samples was measured, and the Cu and Mn contents determined quantitatively; the minimum amount of copper which can be determined by the given method in the samples was found to be 0.03%, while the minimum amount of manganese that can be determined was found to be 0.028%, i.e., the method proved to be sensitive enough.

In Table 2 are given results for the determination of the percentage content of Cu and Mn in a series of samples, as found by our technique, and the results of a chemical method. The statistical error of a measurement did not exceed 5%. By making repeated measurements, a fairly good agreement between results was obtained – of the order of 3%.

In conclusion, it should be pointed out that further improvements in the technique developed for the quantitative determination of Cu and Mn in ores would make it possible to carry out a quantitative determination of these elements during coreless drilling of prospecting wells in the deposits in the republic.

An increase in the power of the neutron flow by increasing the activity of the neutron source, or the use of a slit neutron generator [10], would allow the duration of irradiation to be decreased and the sensitivity of the radioactivation method to be increased.

SUMMARY

The direct determination of 0.03-0.9% of Cu and 0.028-0.3% of Mn is possible with the use of a γ-ray scintillation spectrometer for recording the γ radiation of activated rock samples at a neutron flux of about 10^7 neutrons/$cm^{-2} \cdot sec^{-1}$. The possible experimental error is ±5-8%.

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PHOTOMETRIC DETERMINATION OF THE RARE EARTHS BY MEANS OF SALICYLFLUORONE

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The reagent arsenazo I, suggested by Kuznetsov [1], is widely used for the photometric determination of the rare earths. The present article is devoted to the description of the photometric determination of the rare earths with a new reagent – salicylfluorone [9-(o-hydroxyphenyl)-2 ,3 ,7-trihydroxyfluorone]. Salicylfluorone has been suggested by Nazarenko and Shustova [2] for the photometric determination of thorium and sulfates. In almost neutral solutions, salicylfluorone forms with the rare earths compounds with a maximum absorption at 530 mμ (just like thorium). The compounds obtained (red in color) are stabilized as a suspension in solution by means of gelatin.

The optimum pH value for obtaining the maximum color of solutions of the complexes of the rare earths with salicylfluorone was established as follows. The original weakly acid solutions (pH 3) contained 10 μg Ce_2O_3 per ml and 9 μg Y_2O_3/ml. Into 5-6 25-ml standard flasks, in one series of experiments, were introduced 30 μg lots of Ce_2O_3, and the same amount of Y_2O_3 in another series; 2 ml of a 0.2% alcoholic solution (50% ethanol) of salicylfluorone was added to each flask, followed by 0.5 ml of a 1% gelatin solution, 20 ml of an acetate buffer solution (with given pH values ranging from 3.5 to 7), and the solutions made up to the mark with water. After 30 min, the pH was measured with a potentiometer, and the optical density then measured on an FÉK-N-54 apparatus at 530 mμ in a 20 mm cuvette. Two ml of salicylfluorone solution, to which the gelatin solution and a buffer solution was added, served as the reference solution.

Cerium (Fig. 1) forms a colored compound with salicylfluorone at a higher pH than yttrium. The optical density of solutions of cerium and yttrium salicylfluoronates is most stable at pH 6.7-6.8.

In our subsequent work the buffer solution used was a 20% solution of urotropine – 4 ml to 25 ml of solution (pH 6.7-6.8). A study of the solutions of the complexes formed between the metals and salicylfluorone was carried out at this pH. At higher pH values the optical density of the reagent itself increases, and this is undesirable.

The molar extinction coefficient of solutions of the salicylfluorone complexes of the rare earths was established by the "saturation" method at pH 6.8; it was found to have an average value of 17,500 for cerium, samarium, and lutecium.

The amount of salicylfluorone necessary for maximum development of the color of the cerium complex was found to be 0.75-1 ml per 25 ml of solution (Fig. 2). One ml of the 0.2% salicylfluorone solution should therefore be taken for 25 ml of test solution.

During the photometric determination of total rare earths in ores and rocks, large errors are not obtained under conditions where one or two of the elements are found in the total rare earths in predominating amounts [3]. For example, rare earth oxides of the cerium group usually contain 40% cerium and 25% lanthanum, which have atomic weights of 140.13 and 138.92, respectively; thus the "mean" atomic weight of the elements of the cerium group is close to 140. The atomic weight of the rare earths of the yttrium group "approximates" to 140; yttrium

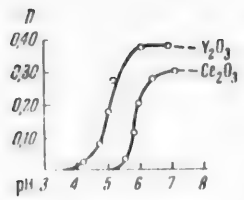

Fig. 1

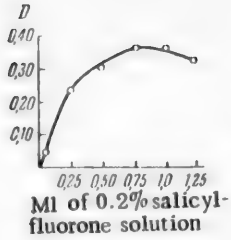

Fig. 2

with an atomic weight of 88.32, and also heavy elements with an atomic weight of 150-175. Depending on the amount of yttrium in the total rare earths, the mean atomic weight can vary by 5-10 units. Normal contents of yttrium in ores and rocks, up to 10-15%, do not appreciably change the mean atomic weight of 140.

With salicylfluorone, just as with arsenazo, yttrium increases the optical density of the solution almost twice as much as cerium (Fig. 3). When yttrium predominates in the rare earths (Fig. 4), the slope of the calibration curve will also sharply differ from that of the line obtained for rare earths of the cerium group. In Fig. 4 are shown calibration curves for the cerium and yttrium groups. The

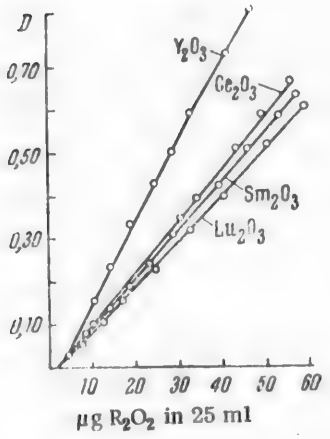

Fig. 3.

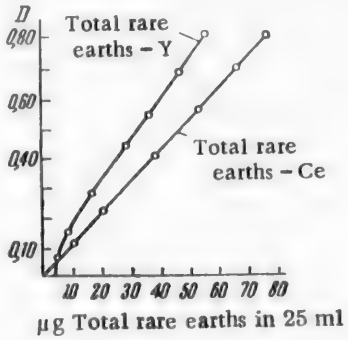

Fig. 4.

composition of the main rare earth oxides (in %), as determined by the usual oxalate method in monazite, was found to be: La_2O_3 – 27.81; CeO_2 – 41.72; Pr_6O_{11} – 6.62; Nd_2O_3 – 10.6; Sm_2O_3 – 4.63; Gd_2O_3 – 3.30; and that of the yttrium group from xenothyme Y_2O_3 – 61.8; Er_2O_3 – 8.01; Lu_2O_3 – 9.8; Tb_4O_7 – 1.5; Sm_2O_3 + Gd_2O_3 – 6.7; Nd_2O_3 – 8.4; Pr_6O_{11} – 2.3; CeO_2 – 2.1; La_2O_3 – 1.6. Solutions containing 10 μg total rare earths/ml (pH 3) were prepared from the rare earth oxides (by dissolving an aliquot in concentrated hydrochloric acid). With low contents of down to 10-15% of yttrium in the total rare earths, the tangents of the calibration curves for the cerium or yttrium groups do not differ sharply. Under such conditions, it is still possible to carry out photometric determinations of the total rare earths of the cerium and yttrium groups with salicylfluorone.

Sodium ethylenediaminetetraacetate, sulfosalicylic acid, etc., do not strongly affect the color of suspensions of the complexes formed between salicylfluorone and the rare earths. Calcium and magnesium form colored compounds with salicylfluorone, but they are masked by sulfosalicylic acid (0.5 ml of a 10% solution to 25 ml) and do not interfere with determination of the rare earths. This is the essential advantage of this reagent over arsenazo. It is difficult to mask calcium with sulfosalicylic acid during the reaction of the former with arsenazo [3]. Calcium always accompanies the rare earths, and, moreover, it is used as a coprecipitant in the oxalate method. Removing interference on the part of calcium often complicates analytical methods of determining the rare earths.

It is clear from Table 1 that the rare earths can be determined in the presence of large amounts of calcium (15 mg in 25 ml) with reasonable accuracy and reproducibility. Aluminum* does not form colored compounds with salicylfluorone. Tri- and divalent iron, and quadrivalent titanium, under the conditions used for determining the rare earths with salicylfluorone, form a red colored compound, solutions of which conform to Beer's law (Fig. 5). The reactions for these metals are very sensitive (0.005 μg/ml). Thorium, zirconium, and uranium form compounds with salicylfluorone; the solutions of these compounds also conform to Beer's law (Fig. 6).

*In almost neutral solutions, aluminum reacts with arsenazo to give a colored compound.

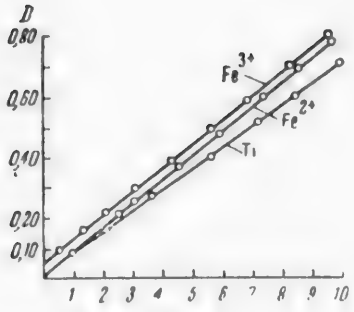

Fig. 5.

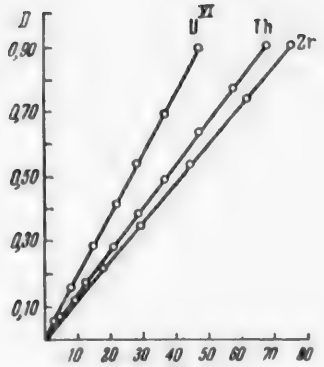

Fig. 6.

TABLE 1

Determination of Total Rare Earths in the Presence of Calcium

Taken in 25 ml		Total rare earths found, μg	Error in determination of the rare earths, μg
total rare earths, μg	Ca, mg		
10	10	9,2	−0,8
10	15	10,8	+0,8
20	10	18,1	−1,9
20	15	22,0	+2,0
50	10	52,0	+2,0
50	15	55,0	+5,0

TABLE 2

Determination of Rare Earths in Magnesium and Barium Alloys

Wt. of alloy, mg		Rare earths found, %		Error (relative), %
		by a gravimetric method	by the given method	
Ba—Ce	10,0	1,52	1,59	+4,60
Ba—Ce	20,0	0,38	0,40	+5,10
Mg—TRE*	10,0	3,00	2,85	−5,26
Mg—Ce	20,0	1,02	0,95	−7,30

* Total rare earths.

During determination of total rare earths in alloys (barium, magnesium alloys), separation of the rare earths from accompanying elements need not be carried out (Table 2). Barium and magnesium ions and traces of divalent iron are masked with sulfosalicylic acid, and do not interfere with determination of total rare earths. In such cases, 10-15 mg of sample is dissolved in 5-10 ml of hydrochloric acid (1 : 1), the solution is neutralized with ammonia to pH 3 using congo red paper; the solution is transferred to a 50 ml standard flask, its volume is made up to the mark with water, and the whole thoroughly mixed.

5-15 ml of the solution obtained is transferred to a 25 ml flask in order to carry out the photometric determination; to the contents of the flask are added 0.5 ml of a 1% solution of ascorbic acid, 0.5 ml of the sulfosalicylic acid solution, 1 ml of a 1% gelatin solution, 2 ml of the 0.2% alcoholic solution of salicylfluorone, and 4 ml of 20% urotropine solution, and the solution made up to the mark with water; the contents are thoroughly mixed and the optical density measured at 530 mμ in a 20 mm cuvette.

A calibration curve is constructed using the reagents indicated and a solution of the total rare earths of the cerium group containing 10-20. . . 70 μg of the rare earths in 25 ml.

It is clear from Table 2 that the rare earths can be determined in alloys by means of salicylfluorone with acceptable accuracy.

SUMMARY

Salicylfluorone forms colored compounds with the rare earths in nearly neutral solutions; solutions of these compounds conform to Beer's law. Salicylfluorone is a more selective reagent than arsenazo I. It is possible to determine certain of the rare earths and their sum photometrically by means of salicylfluorone, sulfosalicylic acid being used for masking calcium and magnesium.

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POLAROGRAPHIC DETERMINATION OF INDIUM IN METALLIC GALLIUM

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Many papers have been devoted to the polarographic determination of indium [1-6]. However, these papers are devoted either to the mechanism of the electrode reaction, or to methods for the determination of indium in the presence of other elements, in particular cadmium, at the usual indium concentrations (10^{-3}-10^{-4} M) for polarographic work. Polarographic methods have not been used for the determination of (10^{-5}-10^{-7}%) indium in high purity metals. The work described here was devoted to establishing the requisite conditions for the polarographic determination of 10^{-5}-10^{-6}% of indium, and also to methods for separating and concentrating indium during the analysis of metallic gallium.

In order to determine indium at a concentration of 10^{-6} M it was essential to choose a suitable supporting electrolyte. Very clearly defined indium waves are obtained in hydrochloric acid solutions, with $E_{1/2}$ equal to, for example in 1 M HCl, 0.60 v (relative to the saturated calomel electrode). With increasing HCl concentration, the half wave potential of indium is shifted to more negative values as a result of complex formation [7]. As our experiments showed, during polarographic examination of 10^{-6}-10^{-7} M indium solutions the HCl concentration not only affects $E_{1/2}$, but also affects the shape of the indium reduction curve, the latter being distorted at HCl concentrations greater than 2 M, while in 6 M HCl the indium wave disappears. 0.2 M HCl was accordingly chosen as the supporting electrolyte. In this region the relation between the value of the diffusion current and the indium concentration is linear over the range 2×10^{-6}- 4×10^{-5} M (Fig. 1). The limiting concentration which can be determined is 2×10^{-6} M indium.

It was also demonstrated that indium can be determined on the GEOKhI oscillograph (Model 2) [8]. In Fig. 2 are shown oscillograms for indium in 0.2 M HCl, and also the curve relating indium peak height and its concentration in solution. As is evident from Fig. 2, the curve is linear from indium concentrations within the range 1×10^{-6}- 2×10^{-5} M. The limiting indium concentration which can be determined by the oscillographic method is 5×10^{-7} M. Thus, it is possible by means of the polarographic method to determine 1×10^{-5}% of indium on a sample weight of 2 g, while by means of oscillographic polarography it is possible to determine 2.5×10^{-6}% In, for a final volume of the solution of not more than 1 ml.

In order to determine indium in gallium it is necessary to carry out a preliminary concentration of the indium.

The method which we suggest for concentrating indium is based on its coprecipitation with cobalt sulfide,* with subsequent removal of indium from gallium** and sulfate ions by extraction of indium with dithizone in the presence of sulfosalicylic acid, or by extraction of indium or gallium with diisopropyl ether.

*Cobalt was chosen as the collector because of its very negative half wave potential.

**About 10% of gallium is coprecipitated with cobalt sulfide.

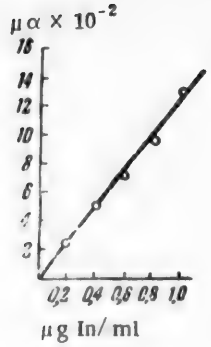

Fig. 1.

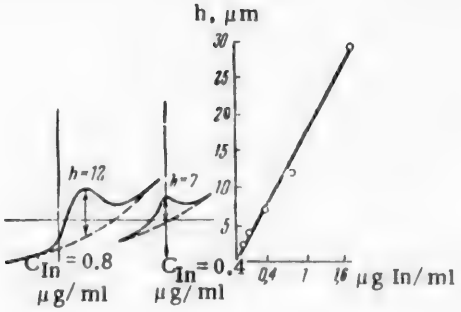

Fig. 2

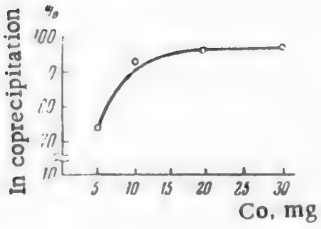

Fig. 3.

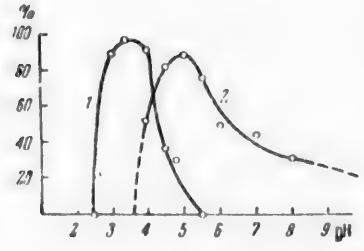

Fig. 4.

As experiments with the radioactive isotope In^{114} showed, by introducing sufficient amounts of cobalt chloride into the solution, indium is coprecipitated quantitatively with cobalt sulfide.

In Fig. 3 is shown the curve illustrating the coprecipitation of 1 μg of indium as a function of the amount of cobalt taken. For cobalt contents ranging from 15 mg upwards, the amount of indium coprecipitated amounts to 95%. In the case of 0.1 μg indium, the percentage coprecipitation is on an average 93% when 10-15 mg cobalt is used.

Of a number of masking agents for gallium (citric, tartaric, malonic acids, etc.) sulfosalicylic acid [9] proved to be the most effective at pH 4.8-5.2. This pH range proved to be the optimum for the quantitative extraction of indium as its dithizonate in the presence of sulfosalicylic acid, as is clear from Fig. 4. The maximum extraction of indium dithizonate in the presence of sulfosalicylic acid is shifted towards higher pH values than occurs with an unbuffered 10^{-3} M solution of indium [10]. It was also established by means of the radioactive isotope In^{114} that indium is quantitatively separated (even 0.1 μg In) from gallium (Ga about 0.1 g) by extracting it with diisopropyl ether from solutions containing HBr. Satisfactory separation of indium from gallium is also possible by extracting gallium with diisopropyl ether from a 6 N HCl* solution (Table 1).

As a result of the work carried out, the following method is suggested for the determination of indium in gallium. A 2-5 g aliquot of metallic gallium is dissolved on boiling in 25-30 ml aqua-regia, the latter being added in portions of about 10 ml.** The solution is evaporated to a volume of 3-5 ml, and, after cooling, 50 ml of distilled water is added. Ten-25 g of tartaric acid is added, the solution is neutralized with a 25% ammonia solution, and the pH adjusted to 7-8. Cobalt chloride solution (0.1 M) is added (1.7 ml per g of gallium***), and the indium coprecipitated with cobalt sulfide by adding 10-25 ml of 0.5 N sodium sulfide; the solution is allowed to stand for 30 min in order for the precipitate to coagulate. The sulfides are centrifuged, washed 3-4 times with a 1% solution of ammonium nitrate. The precipitate is dissolved in concentrated HNO_3 (the latter being added gradually in 3-5 ml lots) and the solution transferred to a 100 ml beaker of heat-resistant glass, in which it is evaporated to dryness. One of the following variants is then employed.

*The indium concentration was determined polarographically.

**Dissolution proceeds slowly.

***This corresponds to 10 mg cobalt.

TABLE 1

Separation of Indium from Gallium by Extracting the Latter with Diisopropyl Ether from 6 N HCl (0.1 g gallium taken)

In added, μg	In found, μg	Error (relative) %
5.0	4.75 *	−5.0
2.5	2.30 *	−8.0
1.0	0.90 *	−10.0

*Mean of three determinations.

TABLE 2

Determination of Indium in High Purity Gallium

In added, μg	i_d, μa × 10^{-2}	In found, μg	Error (relative), %
0,2	2,3	0,18	—10
0,4	4,8	0,39	—3
0,4	4,4	0,36	—10
0,6	6,3	0,51	—15
1,0	11,4	0,91	—9

The residue in the beaker is dissolved in 2-3 ml of concentrated hydrochloric acid, water is added to bring the volume up to 10 ml, 2 g of sulfosalicylic acid is added,* and the pH of the solution adjusted to 4.8–5.2.

The solution is transferred to a 50-100 ml separating funnel and the indium extracted twice with 3-5 ml of a 0.05% solution of dithizone in CCl_4. The CCl_4 layer is removed to another separating funnel, and the collected extracts washed twice with distilled water. 3-5 ml of 2 M HCl is added to decompose the indium dithizonate, the CCl_4 layer is removed and discarded, while the hydrochloric acid solution is evaporated to dryness in a small quartz basin. To the dry residue is added a few drops of concentrated $HClO_4$ and the solution evaporated to dryness on a hot plate (in order to destroy organic matter). The residue is dissolved in exactly 1 ml of 0.2 M HCl; the solution is placed in the electrolyzer and is purged with nitrogen (or hydrogen) for 5-10 min, and polarograms taken over the range 0.2 to 0.8 v at a high galvanometer sensitivity (1/2-1/3). The indium content is determined by means of a calibration curve (Fig. 1). The results given in Table 2 indicate the accuracy of the determination of indium in gallium. The relative experimental error for the determination of 0.2-1.0 μg of indium does not exceed 15%.

The solution obtained can also be analyzed by oscillographic polarography. In this case there is no need to remove the oxygen from the solution, and curves such as those shown in Fig. 2 are obtained. A calibration curve is constructed using solutions of an indium salt with a known concentration. The oscillograms of the standard and test solutions are obtained under the same operating parameters of the instrument [11].

The residue is dissolved in 2-3 ml of concentrated HNO_3, 2-3 drops of bromine is added and the solution evaporated to dryness; after cooling, 10 ml of 5 N HBr is added, and the solution evaporated to dryness. The operation of evaporation with HBr is repeated.

The dry residue is treated three times with 3-4 ml of 5 N HBr and the solutions poured into a 25 ml separating funnel. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min. After separating into two phases the aqueous layer is transferred to another 25 ml separating funnel, 10 ml of ether is added and the extraction repeated. The ethereal extracts are combined and washed twice with 5 ml of 5 N HBr. The ethereal solution is placed in a quartz crucible of about 25 ml capacity and is evaporated to dryness on a water bath. The residue is moistened with a few drops of perchloric acid, the crucible is then placed in a muffle and heated to 400-500° for 5-7 min to get a white residue.** Some more drops of perchloric acid is added and the crucible carefully heated on a hot plate until white fumes of $HClO_4$ cease to come off. After cooling, the residue is dissolved in

*This amount of acid is sufficient to complex 0.1 g of gallium.

**If the residue is colored, this operation is repeated.

1 ml of 0.2 M HCl, the solution obtained is transferred to the electrolyzer, and the procedure outlined in the first variant then followed.

The residue is dissolved in 5 ml of 6 N hydrochloric acid and the solution transferred to a 20-25 ml separating funnel; the beaker is washed with 2-3 ml of 6 N HCl. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min; after separating into two phases, the aqueous layer is transferred to another separating funnel and the operation of extracting gallium with the ether repeated twice again, 5 ml of ether being used each time. The ethereal extracts are discarded while the hydrochloric acid solution containing the indium is evaporated to dryness in a quartz basin, the residue is then twice evaporated to dryness with a few drops of perchloric acid (to remove organic matter). The dry residue is dissolved in 0.5-1.0 ml (exactly) of 0.2 N HCl, and either polarograms or oscillograms taken, as indicated in the first variant.

Note. All the reagents should be purified beforehand. The acids and organic solvents should be distilled 2-3 times in quartz apparatus. Chemically pure grade salts should be recrystallized 2-3 times, and then additionally purified by coprecipitation with cobalt sulfide or by extraction with a solution of dithizone in CCl_4. The standard solutions of indium salts and others should be stored in quartz flasks.

The authors express their appreciation to I. P. Alimarin for his valuable assistance in conducting this work.

SUMMARY

Conditions have been developed for separating microgram amounts of indium from gallium by coprecipitating the indium with cobalt sulfide, followed by separation of indium from other components. Polarographic and oscillographic methods of determining indium in metallic gallium are suggested, which permit the determination of 10^{-5}-10^{-6}% of indium with an accuracy of ± 15%.

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POLAROGRAPHIC DETERMINATION OF NIOBIUM, TITANIUM, AND IRON IN METALLIC TANTALUM AND ITS OXIDES

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The methods mainly used in analytical practice for the determination of niobium in the presence of tantalum are photometric methods which involve using the colored compounds formed with pyrogallol or thiocyanic acid [1-3]; under these conditions titanium, iron, and phosphorus interfere; the pH of the medium and the concentration of the reagents added are also of importance. Inaccurate results are obtained during the determination of titanium in the presence of considerable amounts of niobium [4]. Satisfactory results for niobium are obtained only when the optical density is measured in the ultraviolet. Spectrophotometers, however, are not available in all laboratories, and the use of ordinary colorimeters does not always give positive results.

The development of instrumental methods which could be carried out universally for the simultaneous determination of iron, titanium, and niobium without removal of tantalum is a pressing problem. Iron, titanium, and niobium are reduced in a supporting electrolyte of ortho- and pyrophosphoric acids on a dropping mercury cathode, and give well defined polarographic waves, the half-wave potentials of which are well separated from each other, and for which the limiting currents of each element are clearly defined [5-8]. The limiting currents of iron, titanium, and niobium, whether taken separately or in each other's presence, are linearly dependent on their contents in solution over a wide concentration range. These facts have been checked using comparatively large amounts of the elements listed, but the effect of tantalum (particularly at high concentrations) in solutions containing high contents of iron, titanium, and niobium has not been studied at all.

The present article is devoted to a description of a polarographic method for the determination of small amounts of iron, titanium, and niobium in metallic tantalum and its compounds.*

Pyrophosphoric acid (sp.gr. 1.9) was prepared from orthophosphoric acid (chemically pure grade) by means of a well known procedure [9]. Phosphoric acid solutions of titanium, niobium, and tantalum were prepared by fusing aliquots of their oxides with potassium bisulfate and dissolving the melt in sulfuric acid. The metal hydroxides were precipitated from this solution with ammonia, and, after their removal by filtration, were dissolved in pyrophosphoric acid (sp.gr. 1.9). Solutions were also prepared by dissolving aliquots of the oxides in hydrofluoric acid (40%), followed by removal of the hydrogen fluoride by heating the solutions with phosphoric acid until fumes of hydrogen fluoride and water ceased to be evolved.

Polarograms were taken on the SGM 8 polarograph made by the "Geologorazvedka factory." Electrolysis was carried out on a dropping mercury cathode ($m^2/_3\ \tau^1/_6 = 0.94\ mg^{2/3}\ sec^{1/2}$). The galvanometer sensitivity was 0.03 $\mu\alpha$ per mm of the scale. An internal mercury anode was used. The polarograms were taken at 25°.

A study of the polarographic behavior of small amounts of trivalent iron and quadrivalent titanium in the presence of tantalum was carried out in a supporting electrolyte of pyrophosphoric acid of varying concentrations. It was shown experimentally that curves with the best shape were obtained on using a ratio of $H_4P_2O_7 : H_2O = 2 : 1$ (by volume).

*I. S. Skorynina participated in the experimental work.

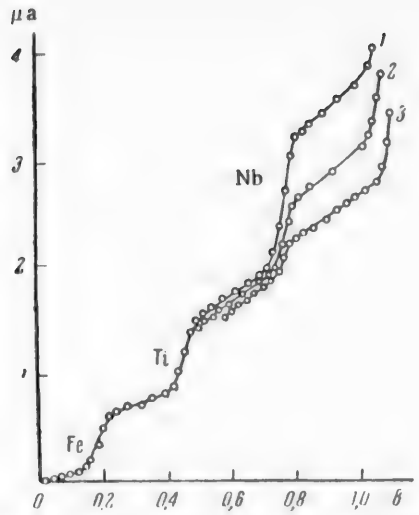

Fig. 1. Polarograms of trivalent iron. quadrivalent titanium, and quinquevalent niobium. Supporting electrolyte, pyrophosphoric acid (sp.gr. 1.85). Niobium contents: 1) 0.5%; 2) 0.25%; 3) 0.1%.

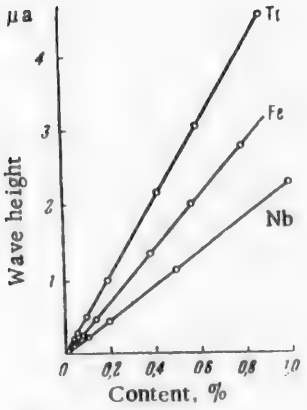

Fig. 2. The limiting current of trivalent iron, quadrivalent titanium, and quinquevalent niobium as a function of their contents in tantalum pentoxide.

Polarograms for trivalent iron and quadrivalent iron and the relationship between their limiting currents and their contents are shown in Figs. 1 and 2.

The direct proportionality between the limiting current of iron and titanium (Fig. 2, curves 1-2) against a background of considerable amounts of tantalum permits the possibility of developing a polarographic method for determining iron and titanium present as impurities in metallic tantalum and in its compounds. The advantage of the method developed is the simplicity with which it can be carried out. The method permits determination of hundredths of a percent of the elements mentioned.

Polarographic determination of niobium present as an impurity in tantalum is possible. Small amounts of niobium in the presence of tantalum give well defined polarograms with $E_{1/2}$ = 0.8 v relative to the internal mercury anode, when a supporting electrolyte of pyrophosphoric acid (sp. gr. 1.9) is used (Fig. 1). The limiting current of niobium is linearly dependent on its concentration in solution (Fig. 2); tantalum ions do not exhibit any influence.

The simplicity of the method developed and its satisfactory sensitivity make it possible to recommend it for the determination of niobium in metallic tantalum and its compounds.

Determination of iron, titanium, and niobium present as impurities in metallic tantalum and its oxide. 0.5-1 g of the metal is dissolved in a platinum basin, as usual in hydrofluoric acid (40%) to which nitric acid has been added. When tantalum oxide is the test material, there is no need to add nitric acid. When the sample has dissolved completely, 20-30 ml of pyrophosphoric acid is added and the solution heated until water vapor, nitrogen oxides, and hydrogen fluoride have ceased to come off. The pyrophosphoric acid solution obtained is transferred to a standard flask (50 or 100 ml) and the volume made up to the mark with dilute pyrophosphoric acid in such an amount that its concentration in the final solution is $H_4P_2O_7 : H_2O = 2 : 1$ (by volume). An aliquot of this solution is used for the polarographic determination of iron or titanium. The electrolysis is carried out using an internal mercury anode.

For the determination of niobium, the pyrophosphoric acid solution is made up to the mark with concentrated pyrophosphoric acid (sp. gr. 1.85-1.9), the solution obtained is carefully mixed and is then used for taking polarograms. Electrolysis is carried out using an internal mercury anode.

It was pointed out above that on a dropping mercury cathode, trivalent iron is first reduced; this is followed by quadrivalent titanium, and finally niobium (Fig. 2). The tantalum present in solution does not affect the diffusion current of the elements being reduced.

Polarographic Determination of Niobium, Titanium, and Iron Present as Impurities in Metallic Tantalum and its Oxide

Nb found, %		Ti found, %		Fe found, %	
by a chemical method [3]	by the polarographic method	by spectrographic method	by polarographic method	by a spectrographic method	by the polarographic method
1.04	1.05	0.33	0.03	0.22	0.21
	1.07		0.03		0.20
	1.04		0.03		0.22
12.8	12.7	0.99	0.98	1.48	1.50
	12.8		0.99		1.49
	12.7		0.97		1.48

Accordingly, favorable conditions are created for the simultaneous determination of iron, titanium, and niobium on one polarogram. In this case, the sample must be prepared in the same way as that indicated for the determination of niobium. During the successive determination of iron, titanium, and niobium, when pyrophosphoric acid (sp.gr. 1.9) is used as the supporting electrolyte, the diffusion rate decreases because of the increasing concentration of the supporting electrolyte; consequently, the diffusion current of iron and titanium falls somewhat. Nevertheless, the sensitivity of the method can be increased by increasing the weight of sample taken, and by using a more sensitive apparatus, e.g., a differential or an oscillographic polarograph.

As is evident from the table the method gives satisfactory results during the simultaneous determination of the elements mentioned in the presence of tantalum.

SUMMARY

Small amounts of iron, titanium, and niobium (0.01-1.0%) give clearly defined polarograms in the presence of a large amount of tantalum (99%) when pyrophosphoric acid is used as the supporting electrolyte; the limiting currents are proportional to the concentration of the elements. A method has been developed for the determination of the metals mentioned, when they are present as impurities in metallic tantalum and its oxide, using only one polarogram; the relative experimental error is ± 3-5%.

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COMPOUNDS OF MOLYBDENUM WITH THIOGLYCOLIC ACID AND A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF MOLYBDENUM

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Thioglycolic acid gives with molybdate a color [1] which is used for its detection [2, 3] and for its photometric determination [4-6]. Ziegler, et al. [7] have noted that the compound formed between molybdenum and thioglycolic acid can be extracted with organic solvents in the presence of tri-n-butylammonium salts. Recently, extraction [8] and chromatographic methods [9] have been suggested for separating molybdenum from vanadium by means of thioglycolic acid.

Richter [4] found, using a photometric method, that sexivalent molybdenum interacts with thioglycolic acid in the molar ratio of 1 : 3. The reaction proceeds according to the following suggested equation:

$$MoO_3 + 3\,HSCH_2COOH = Mo(SCH_2COO)_3 + 3H_2O.$$

Richter is of the opinion that the colored compound formed is a simple salt of trivalent molybdenum with dithioglycolic acid, although this suggestion is not reflected in the formula $Mo(SCH_2COO)_3$. According to Richter, dithioglycolic acid is formed during the oxidation of thioglycolic acid by sexivalent molybdenum. Meyer [10] has advanced the hypothesis, on the basis of Richter's experimental results [4] regarding the molar ratio, that sexivalent molybdenum reacts with thioglycolic acid according to one of the following equations, or according to both simultaneously:

$$2\,MoO_3 + 6HSCH_2COOH = Mo_2\begin{pmatrix} S{-}CH_2COO \\ | \\ S{-}CH_2COO \end{pmatrix}_3 + 6H_2O$$

A salt of dithioglycolic acid

$$2\,MoO_3 + 6\,HSCH_2COOH = Mo_2\left(S\begin{matrix} CH_2COO \\ \diagdown\!\diagup \\ CH_2COO \end{matrix}\right)_3 + 6\,H_2O + 3S$$

A salt of thiodiglycolic acid

Meyer [10] considers that molybdenum is trivalent in these compounds. There is no direct evidence at all in the articles of Richter [4] and Meyer [10] for the reduction of sexivalent molybdenum to the trivalent state. Thioglycolic acid, although it does possess reducing properties, is still not strong enough for one to expect it to reduce sexivalent molybdenum to the trivalent state. It is, apparently, capable under certain conditions of reducing molybdenum to the quinquevalent state only. Such an assumption is confirmed by the fact that thioglycolic acid has been successfully used as a reducing agent for sexivalent molybdenum during its detection by the thiocyanate method [11]. Will and Yoe [5] have pointed out that on increasing the thioglycolic acid concentration (> 0.4% by volume) during the photometric determination of molybdenum, the optical density decreases, probably, as they suggest, as a result of the partial reduction of sexivalent molybdenum by excess reagent with the formation of a colorless complex. Thus a literature review shows that the position with regard to the valence of molybdenum in the compounds formed is not clear; consequently, the composition of these compounds is uncertain,

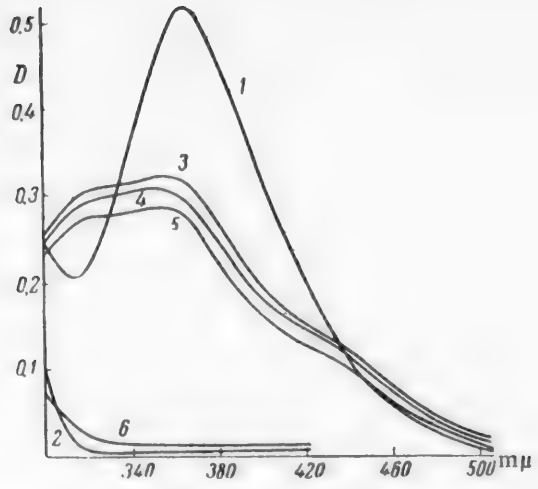

Fig. 1. Absorption curves of solutions of the compounds of thioglycolic acid with sexi- and quinquevalent molybdenum at various pH's. 1) The compound of sexivalent molybdenum, pH 4; 2) thioglycolic acid; 3) the compound of quinquevalent molybdenum, pH 1.78; 4) the compound of quinquevalent molybdenum obtained by mixing solutions of molybdate with thioglycolic acid and adjusting the pH to 0.52; 5) the compound of quinquevalent molybdenum, pH 0.55; 6) dithiodiglycolic acid.

and so is the mechanism of the interaction of molybdate with thioglycolic acid. We set outselves the problem of filling this essential gap in the literature.

EXPERIMENTAL METHOD

The concentration of the aqueous sodium molybdate solution used was established by the 8-hydroxyquinoline method [12]. One ml was found to contain on an average 4.99 mg Mo.

A solution of quinquevalent molybdenum was prepared by reducing a standard hydrochloric acid solution of sodium molybdate with metallic mercury [13], or with hydrazine hydrochloride [14]. In both cases the hydrochloric acid concentration of the final solution was 1 M. Results obtained with both solutions of the quinquevalent molybdenum salt almost coincided.

The trivalent molybdenum salt $(NH_4)_2MoCl_5$ was prepared as described earlier [15].

The concentration of aqueous solutions of a commercial preparation of thioglycolic acid was established iodometrically [16] at various acidities of the solution. The molar concentration of the thioglycolic acid solution was found to be: 0.2061 M (pH 3), 0.02067 M (2 M HCl), 0.02071 (0.4 M HCl) and 0.02055 M (0.04 M HCl), giving a mean value of 0.020603 M.

The optical density was measured on a SF-4 spectrophotometer using a layer thickness of 1 cm. The pH of the solution was measured by a LP-5 pH-meter using a glass electrode.

The valence of molybdenum in the yellow colored compounds formed with thioglycolic acid. Our experiments showed that thioglycolic acid and also dithiodiglycolic acid do not interact with trivalent molybdenum [in the form $(NH_4)_2MoCl_5$] at pH 1-4 to form a yellow colored compound. The assumptions of Richter [4] and Meyer [10] are therefore not confirmed experimentally.

Thioglycolic acid interacts with quinquevalent molybdenum [in the form $(NH_4)_2MoCl_5$] at various pH values (from 1 to 6). During this reaction a stable yellow color develops which is somewhat less intense than that which a solution of ammonium molybdate of the same molarity gives. The assumption of Will and Yoe [5] that quinquevalent molybdenum gives a colorless complex with thioglycolic acid is not confirmed experimentally either.

TABLE 1

Molar Extinction Coefficients of the Thioglycolic Compounds of Sexi- and Quinquevalent Molybdenum

Mo^{VI}				Mo^{V}			
Concentration, M	D^{365} $l=1$ cm	ε_M^{365}	pH	Concentration, M	D^{365} $l=1$ cm	ε_M^{365}	pH
$4 \cdot 10^{-5}$	0,171	4300	4,00	$1,2 \cdot 10^{-4}$	0,296	2500	0,84
$1,2 \cdot 10^{-4}$	0,530	4400	4,20	$1,2 \cdot 10^{-4}$	0,283	2400	0,55
$1,2 \cdot 10^{-4}$	0,525	4400	4,80	$2,0 \cdot 10^{-4}$	0,465	2300	0,3*M* HCl
				$2,0 \cdot 10^{-4}$	0,467	2300	0,3*M* HCl
	Mean:	4400			Mean:	2400	

Dithiodiglycolic acid (taken in excess) does not give colored compounds with either quinque- or sexivalent molybdenum for pH values of 1-4 and 1-7, respectively.

It should be pointed out that the compounds of quinquevalent and sexivalent molybdenum with thioglycolic acid differ not only in the intensity of their colors, but also with respect to some other properties.

In a comparatively acid medium (pH < 3) the compound of sexivalent molybdenum with thioglycolic acid is reduced by excess of the latter to the quinquevalent molybdenum compound. On adding alkali to the compound of quinquevalent molybdenum with thioglycolic acid, the yellow color of the compound changes to the red color of an unstable compound, which rapidly breaks down; under these conditions quinquevalent molybdenum is oxidized to the sexivalent state; on subsequent acidification to pH 3-6 of the solution obtained, there appears the yellow color of a compound of sexivalent molybdenum, when the solution contains excess thioglycolic acid.

It is interesting to note that when excess thioglycolic acid is present during the reduction of sexivalent molybdenum or the oxidation of quinquevalent molybdenum in a weakly acid medium, formation of molybdenum blue is not observed.

Formation of a yellow compound of sexivalent molybdenum with thioglycolic acid is also confirmed by the following experiments. To 2 ml of 0.02 M sodium molybdate solution at pH 1-3 is added 1.0 ml of a very dilute (0.002 M) thioglycolic acid solution, with stirring. The thioglycolic acid is added in a known, lower molar amount with respect to the molybdenum. A distinct yellow color immediately appears. However, after a few minutes, the solution becomes blue because of the formation of molybdenum blue, in which some of the molybdenum is known to be in the quinquevalent state, while some is present in the sexivalent state. When a relatively large excess of thioglycolic acid is used, formation of molybdenum blue is not observed.

Photometric characteristics of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid. The absorption curves of solutions of the compounds of thioglycolic acid with sexi- and quinquevalent molybdenum at various pH values are given in Fig. 1. The solutions were prepared as follows: in a 25 ml standard flask was placed 1.5 ml of a 2×10^{-3} M solution of sodium molybdate or of a quinquevalent molybdenum salt (in 1 N HCl) and a weakly acid (pH 4-5) solution of thioglycolic acid added in such amount that, after dilution, its concentration was 0.4% by volume. The pH of the solution was carefully adjusted by addition of dilute sodium hydroxide or hydrochloric acid solutions, dropwise, with careful stirring. It is necessary to avoid local increases in acid or alkali concentration as much as possible. Only by observing this precaution is it possible to avoid premature, partial reduction of sexivalent molybdenum and oxidation of quinquevalent molybdenum. After this stage the solution was diluted to the mark and its pH measured with a glass electrode. The optical density was measured on a SF-4 spectrophotometer using a cuvette with a layer thickness of 1 cm; the reference solution was a solution prepared in the same way, but omitting molybdenum.

Solutions of the sexivalent molybdenum compound at pH 4 have a maximum absorption at 365 mμ (Fig. 1). The absorption curve of solutions of the compound of sexivalent molybdenum with thioglycolic acid differs from the absorption curve of the compound of quinquevalent molybdenum with thioglycolic acid at pH 4. Solutions

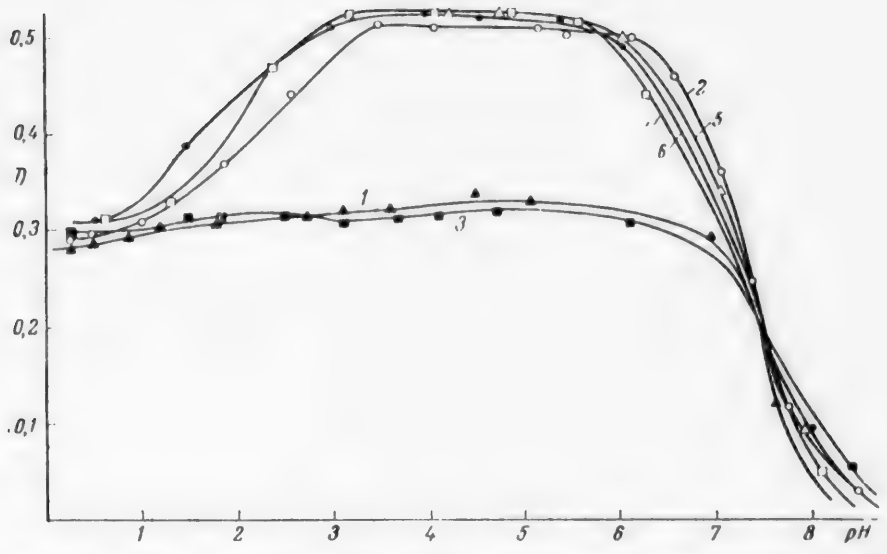

Fig. 2. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid and pH. The final concentrations of sexi and quinquevalent molybdenum were the same and equal to 1.2×10^{-4} M; the thioglycolic acid concentration was constant and equal to 0.4% by volume. 1) Mo^{V} + + $HSCH_2COOH$ at different pH values; 2) Mo^{V} + excess $HSCH_2COOH$; the pH was adjusted to 10 or higher; after 15 min HCl was added to adjust the pH to varying values; 3) Mo^{V} + + excess $HSCH_2COOH$ + HCl until the concentration was 0.5 M; NaOH was added after 15 min to bring the pH to varying values; 4) Mo^{VI} in the presence of excess $HSCH_2COOH$; the solution in Expt. No. 3 was adjusted to pH > 10; after a few minutes HCl was added to bring the pH to varying values; 5) Mo^{VI} + excess $HSCH_2COOH$ (pH of the mixture 4.2), and NaOH added to adjust the pH to varying values; 6) Mo^{VI} + excess $HSCH_2COOH$; NaOH was added to bring the pH > 10; HCl was finally added (after a few minutes) to bring the pH to varying values.

of the quinquevalent molybdenum compound at pH 0.55 and 1.78 have one absorption maximum at 352.5 mμ (Fig. 1). The absorption curves obtained by mixing ammonium molybdate and thioglycolic acid at pH 0.52 and by mixing the compound of quinquevalent molybdenum almost coincide with one another. In both cases the absorption maximum lies at 352.5 mμ. This shows that at pH 0.52 sexivalent molybdenum is reduced by thioglycolic acid to the quinquevalent state; the latter forms a yellow colored compound with excess reagent.

Dithiodiglycolic acid $HOOCCH_2-S-S-CH_2COOH$, which is formed during the reduction of sexivalent molybdenum, does not affect the absorption of the solutions obtained in the operative wavelengths. It starts to absorb light appreciably at wavelengths below 320 mμ (Fig. 1). The dithiodiglycolic acid solution used for obtaining the absorption curve was prepared by oxidizing 1.5 ml of 0.02 M thioglycolic acid with iodine, removing excess of the latter by reduction with $Na_2S_2O_3$, and diluting with water to 25 ml.

The molar extinction coefficient of the thioglycolic compound of sexivalent molybdenum at 365 mμ and at the optimum pH was found to be 4400, while that of the thioglycolic compound of quinquevalent molybdenum was found to be 2400 (Table 1).

Conditions under which compounds of sexi- and quinquevalent molybdenum with thioglycolic acid exist. Of the greatest interest is the establishment of the conditions for reduction of sexivalent molybdenum with thioglycolic acid and establishing the acidity range within which the respective compounds of sexi- and quinquevalent molybdenum exist. In order to get comparable results, the final concentration of sodium molybdate and of the quinquevalent molybdenum salt in all cases was the same (1.2×10^{-4} M), while the thioglycolic acid concentration was always 0.4% by volume. The pH of the solution was adjusted to the requisite value very carefully, as was done during obtaining the absorption

TABLE 2

Reduction of Sexivalent Molybdenum by Thioglycolic Acid on the Basis of the Results of the Iodometric Titration of the Latter

Valence of molybdenum in the original solution	Acidity of the solution	Thioglycolic acid found, mg	Mo found, mg	% Mo^{VI} reduced	Error, %
Mo^{V}	1 *M* HCl	16,09	—	—	—
	0,04 *M* HCl	16,26	—	—	—
	pH 2,42	16,05	—	—	—
	pH 3,78	16,59	—	—	—
Mo^{VI}	1 *M* HCl	12,79	3,559	89,93	—10,07
	0,5 *M* HCl	12,41	3,943	99,61	—0,39
	0,1 *M* HCl	12,44	3,914	98,91	—1,09
	0,05 *M* HCl	12,54	3,809	96,23	—3,77
	pH 1,82	12,45	3,895	98,40	—1,60
	pH 2,47	12,41	3,943	99,61	—0,39
	pH 3,03	14,49	1,775	44,84	—55,16
	pH 3,63	15,92	0,278	7,03	—92,97
	pH 3,98	15,96	0,240	6,06	—93,94

curves. The optical density was measured at 365 mμ relative to water. For solutions with pH 3, the optical density was measured half an hour after preparing them, when the optical density had become constant. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thioglycolic acid (when excess of the latter was present) and the pH of the solutions is shown in Fig. 2. Comparison of Curves 1-6 in Fig. 2 makes it possible to come to a final decision in regard to acidity limits within which compounds of quinque- and sexivalent molybdenum with thioglycolic acid exist, and to solve the question of the conditions under which these compounds mutually change into each other. The thioglycolic compound of quinquevalent molybdenum is formed within a wide acidity range of the solution ranging from 0.5 M HCl to pH 6 (Fig. 2, Curve 1). Under these conditions, the optical density of the solutions is almost independent of the acidity of the solution. On increasing the pH from 6 to 8, a rapid decrease in the intensity of the yellow color occurs.

On increasing the pH of solutions of the compound of quinquevalent molybdenum with thioglycolic acid to pH 10 and above (in the presence of excess thioglycolic acid),* oxidation of quinquevalent molybdenum by atmospheric oxygen or by hydrogen ions occurs. When the solution obtained under these conditions is carefully acidified with hydrochloric acid until the solution is weakly acid (pH 3.5-6), a yellow color appears. The molar extinction coefficient is 4200. The absorption curve of this solution almost coincides with the absorption curve of the compound of sexivalent molybdenum with thioglycolic acid of equal molar concentration. This fact confirms that quinquevalent molybdenum is oxidized to the sexivalent state under the experimental conditions. The compound of sexivalent molybdenum with thioglycolic acid is stable at pH 2.5-6. At pH < 3 sexivalent molybdenum is reduced with thioglycolic acid to the quinquevalent state. Under these conditions the molar extinction coefficient decreases from 4300 to 2500, i.e., to a value which is characteristic for the quinquevalent molybdenum compound.

By altering the pH of solutions containing excess thioglycolic acid, it is possible to convert molybdenum almost quantitatively from the sexivalent state to the quinquevalent state, and the quinquevalent to the sexivalent state. This is confirmed by the agreement found between the values for the molar extinction coefficients for the respective solutions and those found earlier for the sexi- and quinquevalent molybdenum compounds.

The fact that sexivalent molybdenum is reduced quantitatively to the quinquevalent state by excess thioglycolic acid in an acid medium is also confirmed by its iodometric titration. Quinquevalent molybdenum under certain conditions is not oxidized by iodine, and does not appreciably affect the titration of thioglycolic acid (Table 2). To a molybdate solution of known concentration was added excess of a standard solution of thioglycolic acid, which was first neutralized with alkali to a pH of 4-5; the acidity of the solution was adjusted to a definite value, and the solution diluted to 25 ml with water saturated with CO_2; the solution was left for about three hours and the thioglycolic acid solution titrated with iodine solution (0.01 N) using starch as indicator. Near the end point the yellow color of the molybdenum compound was observed to disappear gradually; accordingly, it was

*Thioglycolic acid in excess prevents the hydrolysis of quinquevalent molybdenum. The solution remains clear throughout the whole pH range.

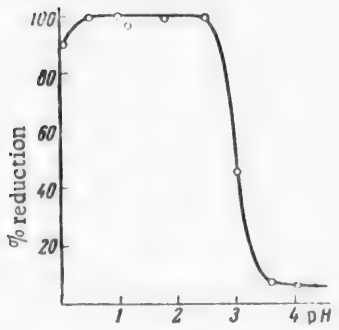

Fig. 3. Effect of acidity of the solution on completeness of reduction of sexivalent molybdenum with thioglycolic acid.

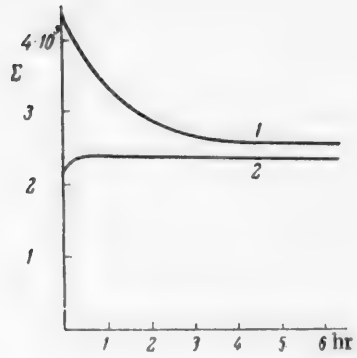

Fig. 4. Effect of standing time on the optical density of solutions of the compound of sexivalent molybdenum with thioglycolic acid, in the presence of excess of the latter. 1) 2% $HSCH_2COOH$ by weight, pH 4.48; 2) 0.4% $HSCH_2COOH$ by volume in 0.3 M HCl.

necessary to shake the solution vigorously after addition of each drop of iodine solution, the drops being added at intervals. Titration was complete when there was a distinct change to blue on addition of a drop of iodine, this color being stable for several minutes. The amount of molybdenum was calculated on the assumption that it was reduced from sexivalent to the quinquevalent state. The results are given in Table 2 and in Fig. 3. From Fig. 3 it is clear that at pH < 2.5 sexivalent molybdenum is completely reduced to the quinquevalent state. Excess reagent forms a colored compound with quinquevalent molybdenum. Our results have justified the use of thioglycolic acid [11] for reducing sexivalent molybdenum during its detection by the thiocyanate method.

In 1 M HCl low results are obtained, probably because of the partial oxidation of quinquevalent molybdenum by iodine at such an acidity. At pH 2.5-3.5, sexivalent molybdenum is incompletely reduced by thioglycolic acid. In a weakly acid medium (pH > 3.5), probably, reduction of molybdenum only proceeds to a negligible amount, and is dependent on the excess concentration of thioglycolic acid. There is a published reference [5] to the fact that at high thioglycolic acid concentrations (> 0.4%), the yellow color arising from the molybdenum complex at pH 4 gradually decreases, and the hypothesis is advanced that the reason for this may be partial reduction of molybdenum by excess reagent with formation of a colorless compound. In our experiments, at high thioglycolic acid concentrations (2% by weight) and at pH 4.48, the optical density, measured relative to water at 365 mμ, gradually changes on standing; this shows that reduction of sexivalent molybdenum under the conditions indicated, proceeds slowly; nevertheless, after four hours, almost all the molybdenum is found in the quinquevalent state. Under these conditions $\varepsilon^{365}_{M} = 2600$ (Fig. 4). After 24 hr the yellow color of the solution has changed to brown, probably as the result of sulfide formation.

In principle it should be possible to determine sexivalent molybdenum by iodometric titration of excess thioglycolic acid.

On the basis of our results it is obvious that at pH 3.5-6 thioglycolic compounds of sexivalent and quinquevalent molybdenum with an intense yellow color exist. At pH > 6, both compounds decompose, the quinquevalent molybdenum changing into the sexivalent stage. At pH < 2.5, only the thioglycolic acid compound of quinquevalent molybdenum is stable. Under such conditions, sexivalent molybdenum changes quantitatively into the quinquevalent state in the presence of excess thioglycolic acid.

The composition of the compounds formed by the interaction of thioglycolic acid with sexi- and quinquevalent molybdenum. The ratio between sexivalent or quinquevalent molybdenum and thioglycolic acid in the colored compounds formed was established by the isomolar series method. Varying volumes of 0.2063 M solutions of sodium molybdate or quinquevalent molybdenum salt (in 1 M HCl) were mixed with an almost neutral 0.02063 M solution of thioglycolic acid so that the sum of the molar concentrations of both components was always constant and equal to 9.90×10^{-4} M. The acidity of the solutions was adjusted by means of a buffer solution with pH 3.6, or by the careful addition of the calculated amount of hydrochloric acid. The optical density was measured

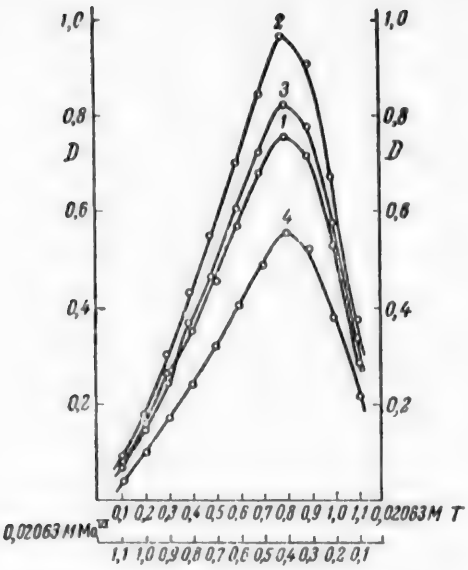

Fig. 5. Interaction of sexivalent molybdenum with thioglycolic acid at pH 3.6. The optical density was measured relative to water. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

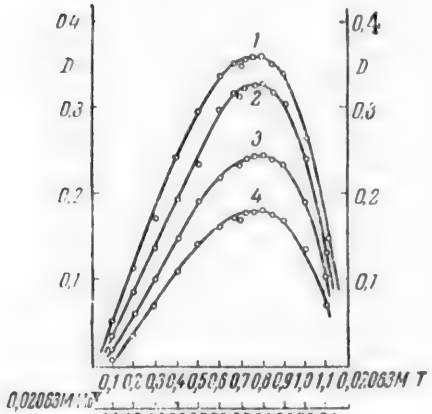

Fig. 7. Interaction of quinquevalent molybdenum with thioglycolic acid in 0.02 M HCl. The optical density was measured relative to solutions of a quinquevalent molybdenum salt of equal concentration in 0.02 M HCl. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

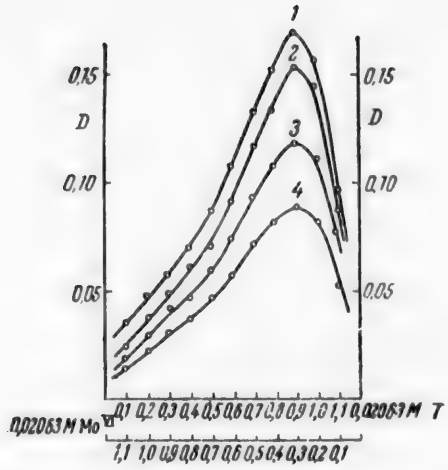

Fig. 6. Interaction of sexivalent molybdenum with thioglycolic acid in 0.02 M HCl. The optical density was measured relative to water. 1) At 345 mμ; 2) at 365 mμ; 3) at 385 mμ; 4) at 405 mμ.

at 345, 365, 385, and 405 mμ. Two series of solutions were prepared in the case of sexivalent molybdenum. In one series the solutions had a pH of 3.6; under these conditions the reaction is instantaneous; the optical density was measured not later than 30 min after mixing; on standing for a longer time some of the solutions become blue. The other series of solutions, which had a constant hydrochloric acid concentration (0.02 M HCl), was allowed to stand for two hours before measuring the optical density in order for the reduction of molybdenum to reach equilibrium. In the experiments with quinquevalent molybdenum, a series of solutions with a final hydrochloric acid concentration of 0.02 M was prepared (taking into account the hydrochloric acid in the original solution). The results obtained are given in Figs. 5-7.

From Fig. 5 it is clear that the maximum optical density (for solutions at pH 3.6) is observed at a molar ratio of Mo^{VI} to thioglycolic acid of 1 : 2. This allows one to write the following equation for the reaction:

$$MoO_2^{2+} + 2HSCH_2COOH = MoO_2(SCH_2COOH)_2 + 2H^+ \quad (1)$$

The maximum optical density in the case of sexivalent molybdenum in 0.02 M HCl is observed at a molar ratio of molybdenum to thioglycolic acid of 1 : 3, i.e., three moles of thioglycolic acid correspond to one mole of molybdate (Fig. 6). Richter [4] obtained the same molar ratio by adding increasing amounts of thioglycolic acid to a molybdate solution (10 mg Mo^{VI}), and measuring the optical density of the neutral solutions which he says he obtained (presumably, the solutions in his experiments were weakly acid). In attempting to repeat Richter's experiments [4] we obtained poorly reproducible and often idefinite results.

Quinquevalent molybdenum interacts with thioglycolic acid in a molar ratio of 1 : 2 (Fig. 7).

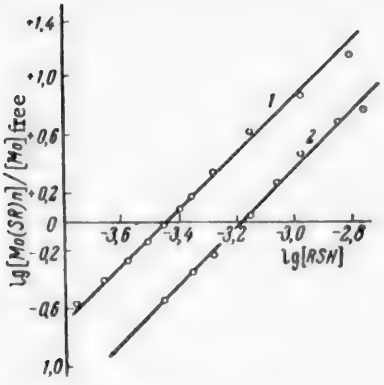

Fig. 8. The relation between $\log([Mo(SR)_n]/[Mo]_{free}$ and $\log[RSH]_{free}$ for solutions of molybdenum compounds with thioglycolic acid. 1) Sexivalent molybdenum; 2) quinquevalent molybdenum.

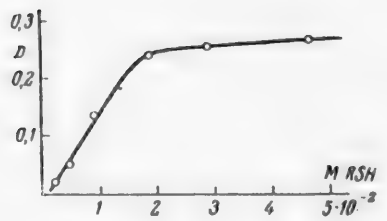

Fig. 9. The effect of thioglycolic acid concentration on the optical density of the solutions. Concentration 1.2×10^{-4} M Mo, 0.3 M HCl; 365 mμ.

By comparing the results obtained it is possible to assume that during the interaction of sexivalent molybdenum in 0.02 M HCl, one mole of thioglycolic acid is used in reducing the molybdate to quinquevalent molybdenum, and then two moles of thioglycolic acid interact with one mole of quinquevalent molybdenum. Thus, it can be regarded as established that in acid solutions the reaction proceeds as follows:

$$2\,MoO_2^{2+} + 6\,HSCH_2COOH = Mo_2O_3(SCH_2COOH)_4 + HOOCCH_2S{-}SCH_2COOH + 4H^+ + H_2O \qquad (2)$$

The molar ratios at which quinque- and sexivalent molybdenum react with thioglycolic acid were also determined by the slope of the lines. The original solutions contained 2.0×10^{-4} M of sexivalent molybdenum and 4.0×10^{-4} M of quinquevalent molybdenum. The optical density was measured at 365 mμ, at which wavelength solutions of quinquevalent and sexivalent molybdenum hardly absorb at all. The optical density of the sexivalent molybdenum solutions was measured as soon as possible after they had been prepared, so that no molybdenum blue was formed in the presence of excess molybdate. Solutions of quinquevalent molybdenum were allowed to stand for two hours in order to attain a constant optical density. The final sexivalent molybdenum solutions had a pH of 3.6. The hydrochloric acid concentration of the final quinquevalent molybdenum solutions was 0.02 M.

When the line slope method was used it was assumed that the reaction proceeds as follows:

$$Mo^{VI,V} + n\,RSH = Mo(SR)_n + nH^+.$$

$$K_{eq} = \frac{[Mo(SR)_n] \cdot [H^+]^n}{[Mo^{VI,V}]_{free}[RSH]^n_{free}}$$

Since the experiments were carried out in solutions with constant acidity, then on taking logarithms of the expression, we get for the constants:

$$n \lg [RSH]_{free} = \lg \frac{[Mo(SR)_n]}{[Mo]_{free}} + \text{const.}$$

When the values of $\log \frac{[Mo(SR)_n]}{[Mo]_{free}}$ are plotted along the ordinate, while the values of $\log [RSH]_{free}$ are plotted on the abscissa, then a straight line is observed. The slope (tangent α) of the straight line will be numerically

TABLE 3

Relation Between $\log \frac{[Mo(SR)_n]}{[Mo]_{free}}$ and $\log [RSH]_{free}$ for Solutions of Molybdenum Compounds with Thioglycolic Acid

Valence of Mo	$[RSH]_{total}$	$D^{365}_{l=1\ cm}$	$[Mo(SR)_n]$	$[Mo]_{free}$	$\log[RSH]$	$\log\frac{[Mo(SR)_n]}{[Mo]_{free}}$
Mo^{VI}	$1{,}76\cdot10^{-4}$	0,185	$4{,}2\cdot10^{-5}$	$15{,}8\cdot10^{-5}$	−3,754	−0,575
	2,20	0,245	5,6	14,4	−3,658	−0,409
	2,64	0,310	7,0	13,0	−3,578	−0,268
	3,08	0,370	8,4	11,6	−3,511	−0,140
	3,52	0,425	9,7	10,3	−3,454	−0,025
	3,96	0,480	11,0	9,0	−3,402	+0,086
	4,40	0,523	11,9	8,1	−3,357	+0,167
	5,28	0,603	13,7	6,3	−3,277	+0,336
	7,04	0,710	16,1	3,9	−3,152	+0,616
	10,56	0,776	17,6	2,4	−2,976	+0,866
	15,84	0,810	18,4	1,6	−2,800	+1,125
Mo^{V}	$3{,}52\cdot10^{-4}$	0,215	$0{,}89\cdot10^{-5}$	$3{,}10\cdot10^{-4}$	−3,454	−0,538
	4,40	0,295	1,23	2,77	−3,356	−0,347
	5,28	0,360	1,50	2,50	−3,277	−0,222
	7,04	0,500	2,08	1,90	−3,152	+0,033
	8,80	0,620	2,58	1,42	−3,055	+0,260
	10,56	0,710	2,96	1,04	−2,976	+0,455
	14,48	0,790	3,30	0,70	−2,839	+0,674
	17,60	0,820	3,42	0,58	−2,754	+0,771

TABLE 4

Determination of Molybdenum in the Presence of Foreign Elements

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error
0,1 Cr ($Cr(NO_3)_3\cdot9H_2O$)	0,60	0,62	+0,02	2,4 Total rare earths oxides	0,38	0,37	−0,01
1,0 Cr ($Cr(NO_3)_3\cdot9H_2O$)	0,60	0,60	0				
1,5 Cr ($Cr(NO_3)_3\cdot9H_2O$)	0,38	0,37	−0,01	29,5 Total rare earths oxides	0,38	0,38	0
10,4 Cr ($Cr(NO_3)_3\cdot9H_2O$)	0,38	0,39	+0,01				
0,5 V (V_2O_5)	0,60	0,60	0	400,0 Thiourea	0,38	0,39	+0,01
1,0 V (V_2O_5)	0,60	0,60	0	1,3 Cu($CuSO_4\cdot5H_2O$)*	0,38	0,38	0
1,7 V (V_2O_5)	0,38	0,41	+0,03	8,4 Cu($CuSO_4\cdot5H_2O$)*	0,38	0,38	0
2,2 Ti ($Ti(SO_4)_2$)	0,38	0,38	0	11,2 Fe($FeCl_3\cdot6H_2O$)**	0,38	0,38	0
18,5 Ti ($Ti(SO_4)_2$)	0,38	0,37	−0,01	3,0 W($Na_2WO_4\cdot2H_2O$)***	0,47	0,47	0

*In the presence of 0.5 g thiourea.

**In the presence of 0.2 g ascorbic acid.

*** After filtering off turbidity of $WO_3\cdot nH_2O$.

equal to n. The results obtained are given in Table 3. From Fig. 8, the slope of line 1 is 1.94, while that of line 2 is 2.0. Accordingly, both quinque- and sexivalent molybdenum interact with thioglycolic acid in molar ratios of 1 : 2 at pH 3.6.

These results coincide with the results obtained by the isomolar series method.

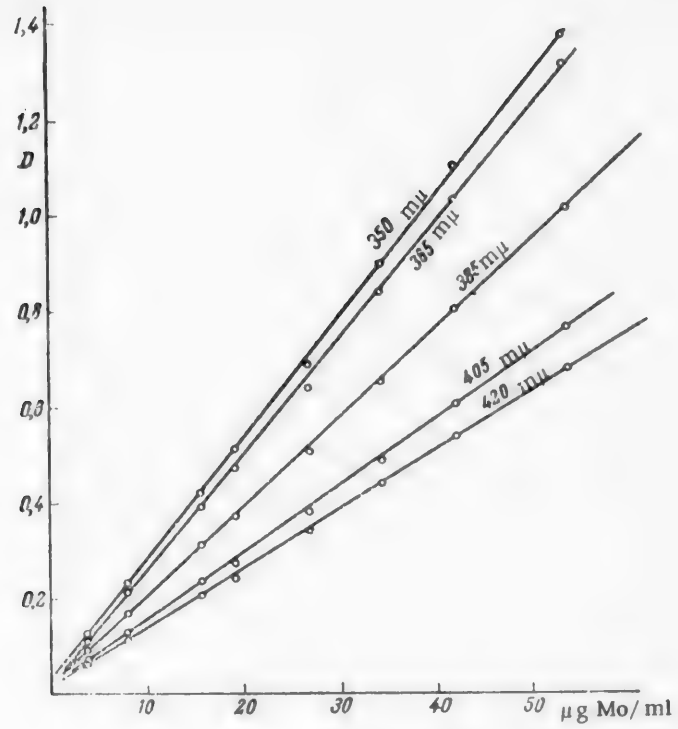

Fig. 10. Calibration curves.

Colored compounds of sexi- and quinquevalent molybdenum with thioglycolic acid (at an acidity corresponding to pH 5.1 and 0.1 M HCl) migrate to the anode, i.e., molybdenum is found in the form of anionic complex compounds.

Sexi- and quinquevalent molybdenum interact with thioglicolic acid, apparently via the sulfhydryl group, not through the carboxyl group.

An improved version of the photometric determination of molybdenum with thioglycolic acid. As already explained, when a large excess of thioglycollc acid is present in moderately acid solutions, the thioglycolic acid completely reduces molybdate to quinquevalent molybdenum, which then interacts with excess reagent to give a fairly intense yellow color. Within the acidity limits pH 2.5 to 0.5 M HCl, the optical density of the solutions obtained is almost constant, while most of the accompanying elements do not form colored compounds with thioglycolic acid under these conditions. In this way it is possible to increase the selectivity of the determination of molybdenum with thioglycolic acid. At a thioglycolic concentration of 2.5×10^{-2} M, the optical density of 1.2×10^{-4} M solutions of molybdenum reaches a maximum value and remains almost constant on increasing its concentration further (Fig. 9). The optical density becomes constant 15 min after preparing the solutions, and does not change in the course of several hours (Fig. 4).

Calibration curve. Ten ml of a standard solution of sodium molybdate containing not more than 1 mg of molybdenum is introduced into a 25 ml flask; 1.3 ml of dilute hydrochloric acid (1 : 1) is added; in this case the HCl concentration in the final solution will be 0.3 M. Two ml of 0.5 M thioglycolic acid solution is then added, and the solution diluted to the mark with water; the whole is thoroughly mixed and the solution allowed to stand for 20 min; the optical density is measured at 365 mμ or 350 mμ with respect to water. The solutions conform to Beer's law (Fig. 10) at 350, 365, 385, 405, and 420 mμ. The method permits determination of molybdate at concentrations ranging from 1 to 40 μg per ml.

Determination of molybdenum in the presence of foreign elements. We have studied the possibility of determining molybdenum in the presence of those elements which interfere with its determination in variants of the thioglycolate method suggested earlier [5]. Experiments with synthetic mixtures were carried out in the same way

TABLE 5

Determination of Molybdenum in a Standard Sample of Steel No. 197 (0.97% Mo, 0.10% Ni, 0.29% Mn, 0.32% Cr, 15.72% W, 0.31% Si)

Sample No.	Mo found, %	Error, %
1	0.99	+ 0.02
	0.98	+ 0.01
2	0.97	0
	0.92	− 0.05
3	0.97	0

as that used for constructing the calibration curve, the only difference being that the solution was first neutralized. The results are given in Table 4.

Copper gives a yellowish precipitate with the reagent under the experimental conditions and interferes with molybdenum determination. Nevertheless, even large amounts of copper do not interfere, if it is complexed with thiourea. Large amounts of trivalent iron do not interfere with the determination if it is first reduced to the divalent state with ascorbic acid (under these conditions, the molybdate is also reduced to the quinquevalent state); accordingly there is no need to remove molybdenum from iron during the determination of molybdenum in steel. Tungstate does not give a color with the reagent, but at 0.3 M HCl it separates out as a precipitate or in the form of a suspension. The precipitated tungstic acid strongly affects the optical density; accordingly, it must be filtered off through filter paper. When large amounts of tungstate are present, high results are obtained for molybdenum if the solution is allowed to stand for a long time. Quadrivalent vanadium is masked by sodium fluoride at pH 2, and a colorless solution is obtained. Univalent mercury gives a black precipitate with the reagent and interferes with the determination. Large amounts of chromium, titanium, and rare earths do not interfere with molybdenum determination. Compared with the method in which molybdenum is determined at pH 3-5 by means of thioglycolic acid, the method which we recommend has a higher selectivity, does not necessitate separation of molybdenum from iron, and ensures that a color which is stable with time is obtained; this method, however, is less sensitive.

Determination of molybdenum in steel. A sample of steel weighing about 0.25 g is placed in a 100 ml beaker and is dissolved in a mixture of 5 ml HNO_3(1 : 1) and 5 ml H_2SO_4 (1 : 1); the solution is evaporated to the appearance of white H_2SO_4 fumes. If the steel does not dissolve completely, a few ml of HCl (1 : 1) is added and the solution evaporated to dryness; this operation is repeated several times until the steel has dissolved. After cooling, 20 ml of water is added and the solution heated to dissolve the salts. Insoluble silicic acid is filtered off on a filter paper, the filter paper plus precipitate are washed several times with the minimum amount of water, and the filtrate collected in a 50 ml standard flask. After cooling, the solution is diluted to the mark with water, and a suitable aliquot of this solution pipetted into a 25 ml flask. Ascorbic acid (0.2 g per 10 mg iron) is added, and, after a few minutes, most of the acid is neutralized with alkali (to pH 2-3 according to universal indicator paper). The procedure subsequently followed is the same as that used for constructing the calibration line. When the steel contains tungsten, the tungstic acid which separates out must be removed by filtration.

Satisfactory results have been obtained during the determination of molybdenum in a standard sample of steel No. 197 (Table 5).

SUMMARY

Under certain conditions, molybdenum, both in the quinque- and sexivalent state, forms a yellow colored compound with thioglycolic acid. Maximum absorption is observed at 352.5 and 365 mμ, respectively, while

the respective molar extinction coefficients are 2400 and 4400. Molybdenum in both valence states interacts with thioglycolic acid (R) in equal molar ratios of Mo : R = 1:2. Trivalent molybdenum does not give a yellow colored compound with thioglycolic acid.

The stability of the compounds of quinquevalent and sexivalent molybdenum with thioglycolic acid depends on the acidity of the solution. In moderately acid solutions (pH < 2.5) the compound of sexivalent molybdenum with thioglycolic acid is unstable, and reduction of sexivalent molybdenum by thioglycolic acid to the quinquevalent state occurs, with formation of the corresponding compound with excess thioglycolic acid. The compound of quinquevalent molybdenum obtained is stable in acid solutions (pH 0.7-6). Molybdenum is only completely reduced to the quinquevalent state by thioglycolic acid in an acid solution. In weakly acid media (pH 2.5-6) sexivalent molybdenum is slowly reduced by thioglycolic acid to the quinquevalent state, only in the presence of a very large excess of reagent. In the absence of a large excess of reagent, the sexivalent molybdenum compound is fairly stable at pH 2.5-6. On increasing the pH there is an increased tendency for the quinquevalent molybdenum compound with thioglycolic acid to be oxidized to the sexivalent state.

The selectivity of the reaction of quinquevalent molybdenum with thioglycolic acid in a weakly acid medium (in 0.3 M HCl) is considerably higher than the selectivity of the reaction with sexivalent molybdenum at pH 3-5. The sensitivity of the reaction is, however, lower. A highly selective photometric method has been developed for the determination of small amounts of molybdenum (1-40 μg Mo/ml) in alloyed steels. Vanadium and large amounts of titanium, the rare earths, iron, copper, and tungsten do not interfere.

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COMPLEXONOMETRIC TITRATION OF QUADRIVALENT URANIUM USING THORON AS INDICATOR

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The stability of the complex compound of uranyl with sodium ethylenediaminetetraacetate (EDTA-Na) is low. EDTA-Na is used mainly as a masking agent during the separation of uranium from many elements by precipitation [1-3], extraction [4-7], and chromatography [8, 9], and also during the determination of uranium gravimetrically [3, 10-14], photometrically [15-18], and polarographically [19]. The uranyl ion forms a stable compound with EDTA-Na at pH 3.5-4.0. In contrast to other metals which react with EDTA-Na in the proportion of 1 : 1, in the given instance two atoms of uranyl correspond to one molecule of the EDTA [20-21].

In pure solutions, UO_2^{2+} ions can be determined by high frequency complexonometric titration [20]. Takomoto [22] has tried to determine uranyl ions by back titration in an acetate buffer solution by means of the salt of divalent cobalt and potassium thiocyanate, but he did not obtain satisfactory results. Lassner and Scharf [23] have suggested a rapid method for titrating uranyl ions at pH 4.4-4.6 with EDTA-Na solution, using 1-(2-pyridylazo)-2-naphthol as indicator; titration is carried out in a 1 : 2 mixture of water and isopropanol.

Quadrivalent uranium forms a very stable, soluble, complex compound with EDTA-Na, and uranium is not precipitated from solutions of this compound by means of ammonia. This fact has been used for separating quadrivalent uranium from titanium and beryllium [24]. The complexonometric method of determining quadrivalent uranium is based on boiling a solution of uranyl acetate with excess EDTA-Na at pH 3-4 in the presence of ascorbic acid, which acts as a reducing agent, and titrating excess EDTA-Na with thorium nitrate solution in the presence of xylenol orange at pH 2-3 [25].

The aim of the work described here was to find a suitable indicator for the complexonometric titration of quadrivalent uranium.

Alizarin red S gives a red color with quadrivalent uranium in acid media [26]. We tried to use it as an indicator for the complexonometric titration of quadrivalent uranium, but it was found that the red color disappears too soon – before the equivalence point is reached.

Pyrocatechol violet (pyrocatechol sulfophthalein) forms colored complex compounds with tri- and quadrivalent cations in acid media, while it only forms colored complex compounds with divalent metals in alkaline media. Pyrocatechol violet has been successfully used for the complexonometric determination of thorium [27, 28] and bismuth [29, 30]. Quadrivalent uranium forms a red compound with pyrocatechol violet at pH < 1.8, while at pH > 1.8 a violet colored compound is formed. We have used pyrocatechol violet as an indicator at pH 1.0-2.0, but we found that the color changes before the equivalence point.

Thoron (benzene-2-arsonic acid-<-1-azo-1->-2-hydroxy-naphthalene-3,6-disulfonic acid) forms a rose colored compound with quadrivalent uranium [31]; it has been used for the photometric determination of uranium [32, 5]. The stability constant of this compound is equal to $9.2 \pm 0.5 \times 10^9$ [32]. Thoron is used as an indicator during the complexonometric determination of bismuth at pH 1.3 [33].

TABLE 1

Determination of Uranium with Thoron as Indicator at pH 1.5

U^{IV} taken, mg	Amount of EDTA-Na solution used, ml	U^{IV} found, mg	Error		Notes
			mg	%	
9,85	4,60	9,86	+0,01	0,1	Titration with 0.0090 *M* EDTA-Na solution
19,70	9,17	19,66	—0,04	0,2	
29,55	4,56	29,50	—0,05	0,2	» 0,0270 *M* The same
39,40	6,10	39,20	—0,02	0,5	
50,20	4,67	50,35	+0,15	0,3	» 0,0453 *M* » »
5,02	7,76	4,99	—0,03	0,6	
3,01	4,67	3,00	—0,01	0,3	
2,01	3,15	2,00	+0,01	0,5	» 0,0027 *M* » »
1,00	1,55	1,00	±0	0	
0,50	7,78	0,50	±0	0	
0,30	4,69	0,30	±0	0	
0,20	3,04	0,195	—0,005	2	» 0,00027 *M* » »
0,10	1,60	0,103	+0,003	3	

TABLE 2

Effect of Acidity on Titration when Thoron is Used as Indicator

U^{IV} taken, mg	Amt. of 0.0027 M EDTA-Na solution used, ml	pH	U^{IV} found, mg	Error	
				mg	%
5,02	7,72	1,0	4,98	—0,04	0,8
3,01	4,68	1,0	3,01	±0	0
2,01	3,11	1,0	2,00	—0,01	0,5
1,00	1,54	1,0	0,99	—0,01	1,0
5,02	7,08	2,0	4,55	—0,47	9
2,01	2,85	2,0	1,83	—0,19	9
5,02	7,76	1,8	4,99	—0,03	0,6
3,01	4,67	1,8	3,00	—0,01	0,3
1,00	1,55	1,8	0,996	—0,004	0,4
5,02	7,76	0,8	4,99	—0,03	0,6
3,01	4,70	0,8	3,02	+0,01	0,3
2,01	3,10	0,8	1,994	—0,016	0,8
2,01	—	0,5			
1,00	—	0,5			

In the work described here we studied the requisite conditions for the use of thoron as an indicator during the complexonometric titration of quadrivalent uranium.

Quadrivalent uranium was prepared by reducing uranyl on a mercury cathode in dilute perchloric acid.

As is evident from Table 1, amounts of uranium from 0.1 to 50 mg are titrated satisfactorily at pH 1.5. At uranium concentrations greater than 0.5 mg/ml of solution, the solution acquires a green-brown color, as a result of which it is difficult to detect the titration end point. It was found that a distinct color change could be obtained at the end point by adding 6-10 drops of a 0.1% solution of indicator while warming the solution (30°).

During a study of the effect of acidity on the titration of quadrivalent uranium, the pH was measured on completion of titration with a glass electrode using an LP-5 potentiometer. Good results are obtained at pH 1.0-1.8 (Table 2). Increasing the pH to 2.0 causes the color change to occur before the titration end point. On dropping the pH to 0.8 the color change becomes indistinct, while at pH 0.5 the rose color hardly changes at all even on adding a considerable excess of EDTA-Na; this is explained by the fact that in more acid media the compound of quadrivalent uranium with EDTA-Na is less stable than that with thoron.

It is clear from Table 3 that the alkali and alkaline earth elements, zinc, divalent manganese, aluminum, lead, lanthanum, and cadmium do not interfere with the titration.

Thorium and bismuth interfere with the titration, since, under the given conditions, they react with EDTA-Na and form rose colored compounds with thoron.

Zirconium also forms a rose colored compound with thoron, and a precipitate is formed on adding a solution of a zirconium salt to the solution being titrated; a similar phenomenon is observed during the photometric titration of zirconium with thoron [34].

Quadrivalent titanium decreases the distinctness of the color change at the end point, since it reacts with thoron to form a rose-orange colored compound. Trivalent titanium, as a strong reducing agent, destroys the indicator and the solution becomes colorless.

TABLE 3

Effect of Various Elements on the Titration of Quadrivalent Uranium with EDTA-Na Using Thoron as Indicator at pH 1.5

U^{IV} taken, mg	Foreign ions taken, mg	0.0090 M EDTA-Na used, ml	U^{IV} found, mg	Error	
				mg	%
10,04	Al 200	4,60*	10,08	+0,04	0,4
9,85	Th 5	6,58	14,11	+4,26	43,0
9,85	La 5	4,61	9,88	+0,03	0,3
9,85	Cd 5	4,58	9,82	−0,03	0,3
9,85	Zn 5	4,60	9,86	+0,01	0,1
9,85	Ce^{4+} 5	4,91	10,53	+0,70	7,0
10,04	Ce^{3+} 2,5	4,68	10,04	±0	0
10,04	Mn^{2+} 20	4,68	10,04	±0	0
10,04	Mg 100	4,67	10,02	−0,02	0,2
10,04	Ca 100	4,68	10,04	±0	0
9,85	Cr^{3+} 5	4,61	9,88	+0,03	0,1
10,04	Ti^{IV} 5	1,56**	10,03	−0,01	0,1
9,85	Fe^{3+} 5	4,60	9,86	+0,01	0,1
10,04	Fe^{2+} 50	4,61*	10,10	+0,06	0,6
10,04	Fe^{2+} 100	5,27*	11,54	+1,50	15
9,85	Co 5	4,71*	30,27	+20,42	200
9,85	Ni 5	1,76**	11,31	+1,46	15
10,04	Ni 2,5	4,68	10,04	±0	0
9,85	Cu 5	4,03**	25,90	+16,05	160
10,04	Bi 5	3,22**	20,70	+10,66	100
10,04	Hg^{2+} 5	3,13**	20,11	+10,07	100
10,04	Pb 20	4,69	10,06	+0,02	0,2
10,04	V 1,0	3,84	8,23	−1,81	18
10,04	AsO_4^{3-} 2,5	2,78	10,25	+0,21	2,0
10,04	AsO_4^{3-} 1,0	4,68	10,04	+0	0
10,04	CH_3COO^- 1 *M* 2 ml	4,69	10,06	+0,02	0,2
10,04	F^- 1	4,04	8,66	−1,38	14
10,04	NaCl 2 g	4,59*	10,05	+0,01	0,1
10,04	$NaNO_3$ 2 g	4,60*	10,08	+0,04	0,4
10,04	Na_2SO_4 2 g	4,62*	10,12	+0,08	0,8
10,04	Na_2SO_4 1 g	4,60*	10,08	+0,04	0,4

*Titration carried out with 0.0092 M EDTA-Na solution.

**Titration carried out with 0.0270 M EDTA-Na solution.

Cobalt, copper, and mercury interfere most strongly, since they also react with EDTA-Na. Vanadium interferes with the titration, since it is reduced during electrolysis to the divalent state, and destroys thoron.

Trivalent cerium, nickel up to 2.5 mg, and divalent iron up to 50 mg do not affect the titration.

Trivalent chromium forms a very stable compound with EDTA-Na [35], but since the reaction between them proceeds slowly, chromium does not interfere with the titration.

Divalent tin interferes since it is hydrolyzed to give a precipitate which adsorbs the indicator. In the presence of molybdate and tungstate blue and yellow precipitates similar to the compound of thorium with molybdenum separate out [36]. Arsenate interferes with the titration even at low concentrations (1 mg); it is very difficult to detect the titration end point in this case.

Nitrate, chloride, and acetate do not interfere with the titration. When sulfate is present the color change is indistinct, particularly at low uranium concentrations. Fluoride interferes fairly strongly, but interference on its part can be eliminated by adding an aluminum salt.

As a result of the experiments we have carried out the following method has been developed for the determination of uranium.

TABLE 4

Masking of Fluoride Ions by Means of Aluminum during the Complexonometric Titration of Quadrivalent Uranium Using Thoron as Indicator (10.04 mg U taken)

0.0092 M EDTA-Na solution used, ml	Fluoride ion added, mg	Aluminum added, mg	U^{IV} found, mg	Error	
				mg	%
4,58	5	100	10,03	—0,01	0,1
4,59	5	100	10,05	+0,01	0,1
4,59	20	200	10,05	+0,01	0,1
4,60	20	200	10,08	+0,04	0,4
4,59	30	200	10,05	+0,01	0,1
4,61	30	200	10,10	+0,06	0,6
4,61	50	200	10,10	+0,06	0,6
4,63	50	200	10,14	+0,10	1,0

TABLE 5

Determination of Uranium in its Tetrafluoride Using Thoron as Indicator

U^{IV} taken, mg	EDTA-Na solution used, ml	U^{IV} found, mg	Error		Notes
			mg	%	
Perchloric acid medium					
19,98	9,12	19,97	—0,01	0,05	Titration with 0.0092 M EDTA-Na solution
19,98	9,14	20,01	+0,03	0,15	
9,99	4,55	9,96	—0,03	0,3	
9,99	4,57	10,01	+0,02	0,2	
9,99	4,56	9,99	±0	0	
5,00	9,21	4,98	—0,02	0,4	" 0.00226 M "
5,00	9,23	4,99	—0,01	0,2	
4,00	7,38	3,99	—0,01	0,2	
4,00	7,41	4,00	±0	0	
2,00	3,73	2,01	+0,01	0,5	
2,00	3,69	1,99	—0,01	0,5	
2,00	3,70	2,00	±0	0	
Hydrochloric acid medium					
18,65	8,52	18,65	±0	0	Titration with 0.0092 M EDTA-Na solution
18,65	8,51	18,64	—0,01	0,05	
9,32	4,26	9,33	+0,01	0,1	
9,32	4,25	9,31	—0,01	0,1	
4,66	8,63	4,66	±0	0	" 0.00227 M "
4,66	8,63	4,66	±0	0	
3,73	6,88	3,72	—0,01	0,3	
3,73	6,88	3,72	—0,01	0,3	
1,86	3,45	1,86	±0	0	
1,86	3,42	1,85	—0,01	0,5	
1,86	3,46	1,87	+0,01	0,5	

Ten ml of uranyl chlorate in 1 N perchloric acid is reduced electrolytically on a mercury cathode; the solution obtained after electrolysis is transferred to a 50 ml standard flask and diluted with water to the mark. Five ml of this solution is pipetted from the flask, 3 ml of 1 N perchloric acid is added and the volume diluted to 100 ml with water. After adding 6-10 drops of a 0.1% solution of the thoron indicator, the solution acquires a rose color. The quadrivalent uranium is then titrated with EDTA-Na solution (it is best to heat the solution to 30° prior to titration). At the end point the color of the solution changes from rose to orange-yellow.

The method developed has been used for determining uranium in its tetrafluoride.

Uranium tetrafluoride was prepared by precipitation from aqueous solutions according to a published method ([26], p. 30). The precipitate obtained was dried in a desiccator over $CaCl_2$ to constant weight. The quadrivalent uranium content was controlled by titration with ammonium vanadate [37].

Quadrivalent uranium can be determined by direct complexonometric titration using thoron as indicator at pH 1.0-1.8 (Table 2). As is evident from Table 4, fluoride is well masked by aluminum; it is only at a ratio of uranium to fluoride of 1 : 5 that the end point is indistinct, but such a ratio is not often met in practice.

For the determination of uranium in its tetrafluoride, an aliquot (0.2 g) of the latter is dissolved in 10 ml of 1 N perchloric or hydrochloric acid in which 1 g of $AlCl_3 \cdot 6H_2O$ has been dissolved beforehand. After the aliquot has dissolved, the solution is transferred to a 50 ml standard flask and diluted with water to the mark. A known volume of this solution is pipetted from the flask and 3 ml of 1 N perchloric or hydrochloric acid added; the solution is then diluted with water to 100 ml; 6-10 drops of the 0.1% solution of thoron is added and the uranium titrated with 0.01 M or 0.003 M EDTA-Na solution until the color of the solution changes from rose to orange-yellow.

As is evident from Table 5, results for the determination of uranium in its tetrafluoride are completely satisfactory.

SUMMARY

It has been established that it is possible to titrate quadrivalent uranium complexonometrically with thoron as indicator at pH 1.0-1.8; the titration can be carried out in the presence of a number of elements. A method is suggested for the determination of quadrivalent uranium in its tetrafluoride, using aluminum ions for masking the fluoride.

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SPECTROGRAPHIC DETERMINATION OF TRACES OF BERYLLIUM IN URANIUM

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There are three groups of methods for the determination of microamounts of Be [1]: photometric [2-6], fluorescent [2,5], and spectrographic [1, 7]. The first two groups require that Be be removed beforehand from interfering elements. In some cases, in the presence of sodium ethylenediaminetetraacetate (EDTA-Na), it is possible to determine Be directly; uranium, however, forms an unstable complex [8] and will interfere with the determination [9, 10]. Moreover, the sensitivity of these methods (approximately 10^{-4}%) is too low. A published spectrographic method [7] permits determination of beryllium in uranium without preliminary separation, but the sensitivity of this method (10^{-3} and 10^{-4}%) is also too low.

Our problem was to develop a method for determining 10^{-6}% Be in uranium. Several methods are known for separating beryllium and uranium: chromatographic separation of Be, U, and Ti on paper [11], a similar separation using complexons [8, 12], electrochromatographic separation on paper [13], and chromatographic separation on a cation exchange resin using various complexing agents [14-17].

The latter technique would appear to be the most promising for separating small amounts of beryllium from large amounts of uranium.

Experimental part. The test material chosen was a metal sample containing almost 100% of uranium. It was checked spectrographically for its Be content (Be < 0.0001%); from this sample a solution of UO_2Cl_2 was prepared containing 39 g uranium/liter. Aliquots of this solution were taken for the experiments.

The beryllium solution (0.2 μ g/ml) was prepared by dissolving beryllium oxide, chemically pure grade, in hydrochloric acid, evaporating this solution almost to dryness, and then diluting. All the remaining solutions of salts, acids, and alkalis were prepared from chemically pure grade materials.

The particle size of the cation exchange resins KU-2 and SBS which were used was 1 to 0.25 mm; they were given a preliminary treatment to free them from impurities, and were converted into the H-form.

First of all we tried to absorb beryllium alone by means of a cation exchange resin (KU-2 or SBS), leaving the uranyl in solution (pH 3-5) in the form of its oxalate complex. Experiments showed that only 40-50% of the beryllium is sorbed on the resin, the remainder staying in the filtrate with the uranyl. Presumably at high oxalate concentrations, beryllium may be partially complexed.

Separation of beryllium and uranium on a cation exchange resin in the form of their sulfosalicylate complexes. Beryllium is capable of forming a relatively stable complex with sulfosalicylic acid at pH 3-4; UO_2^{2+} ions also give a complex, but at pH ≥ 4.4.

Beryllium and uranium were sorbed together on KU-2 cation exchange resin; the beryllium was then eluted separately with sulfosalicylic acid at a definite pH value; under these conditions the uranyl ion was not eluted.

The optimum separating conditions are as follows: 1) separation is completely satisfactory when the particles of the KU-2 resin have a diameter of 0.25 mm. Reduction of the particle size further slows down the process; 2) the optimum elution rate proved to be 0.5 ml/min; under these conditions there is no rapid superposition of

TABLE 1

Taken		Amt. of eluate, ml	Be found, μg		%, extracted
U, mg	Be, μg		in the eluate	in the regenerate	
450	200	700	185	–	92.5
450	200	700	205	–	102.5
450	100	700	100	–	100.0
450	50	800	Not determined	0.45	99.0
450	50	700	"	1.5	97.0

one zone by another; 3) an important factor is the amount of resin, which, in turn, depends on the aliquot taken and determines the distance between the zones of the elements being eluted (on issuing from the column). It was established that in a column with a diameter of 10 mm, and when a 1 g aliquot is taken, it is necessary to have a minimum of 10 g KU-2 resin in the air dry state; 4) one of the chief factors which determine the separation is the acidity of the eluting solution. The best separation is obtained at pH 3; variations can only be permitted toward lower pH values; at pH > 3 superposition of zones occurs, and uranium starts to come off with the beryllium.

The separation consists of the following: a hydrochloric acid solution (0.6 M HCl) containing uranium and beryllium is passed through a column of KU-2 resin in the H-form at a rate of 0.5 ml/min. Uranium and beryllium are sorbed on the resin. The sorbent is next washed with 50 ml of distilled water. The beryllium is eluted with a 0.025 M sulfosalicylic acid solution with a pH of 3 (adjusted by means of ammonia). During the passage of the eluent, there is observed the formation of a dark violet ring right at the top of the column which gradually proceeds downward; this is determined by the presence of traces of iron. Elution of beryllium occurs simultaneously with that of the sulfosalicylate complex of iron, since a beryllium ring is not detected in the eluate prior to elution. When no iron is present (no ring is observed), elution of the beryllium can be observed by following the change in the pH of the eluate; beryllium starts to come off at pH 2.7-3 and its elution is complete either after elution of all the ring or after the appearance of the reddish color of the uranyl complex with sulfosalicylic acid. The eluate collected prior to the elution of the ring (or up to pH 2.7-3) is rejected, and the second portion of eluate (400-500 ml) is taken for analysis. This eluate is evaporated almost to dryness (in a platinum basin), concentrated sulfuric acid is added, and excess of the latter removed by evaporation. The residue obtained is calcined at 300-400° to burn off carbon; it is then fused with $KHSO_4$ in order to convert the BeO into a soluble state and the melt dissolved in a known volume of water. Depending on the expected amount of beryllium either all the solution or an aliquot of it is taken for analysis. Beryllium is determined by the normal fluorescent method. When the sample taken contains some uranium, after calcining to obtain U_3O_8 the residue is weighed and a spectrographic finish used.

Uranium is desorbed with 2 N HCl, the uranium in the eluate is precipitated with ammonia, and the precipitate obtained is calcined and analyzed spectrographically. The possibility of effecting complete separation was checked using solutions of uranium containing from 10^{-2}-10^{-3}% beryllium. Fully satisfactory results were obtained (Table 1).

In order to check the method at lower beryllium contents (10^{-4}-10^{-6}%), a uranium preparation was used which had been specially purified from beryllium by sorption on KU-2 resin and elution with sulfosalicylic acid.

For determining beryllium in such amounts, it is necessary not only to separate it from uranium, but also to concentrate it in such a way that the beryllium can be determined by the usual methods (fluorescent, spectrographic, etc.). The experimental technique was the same; only the amounts of uranium and accordingly the column dimensions were altered. Two series of experiments were carried out using a spectrographic and a fluorescent finish, respectively.

TABLE 2

Taken		Amt. of eluate, ml		Amt. of precipitate as U, mg	Be obtained, μg	% Extracted
U, g	Be, mg	Be	Be+U			
Be alone eluted (20 mg U added)						
1,5	0,05	510	—	25,4	0,025	50
1,5	0,05	430	—	26,2	0,026	48
Be + U eluted (up to 30 mg uranium)						
1,5	0,05	460	25	27,1	0,03	60
1,5	0,05	370	25	28,4	0,03	60
Be + U eluted (above 30 mg uranium)						
1,2	0,1	325	35	33,1	0,08	80
1,6	0,05	200	30	44,7	0,05	100
1,5	0,05	460	35	38,6	0,06	120
1,5	0,05	220	35	39,9	0,04	80

1) Fluorescent determination. Experiments showed that for contents of 1-0.1 μg of Be in 1 g of U, only 50% of the beryllium is eluted from the resin in 100-200 ml of eluate, and a large amount of eluate is required to eluate it completely. Since on passing further amounts of sulfosalicylic acid solution through the column uranium starts to emerge, the fluorescent method is inapplicable; only a spectrographic finish is possible.

2) Spectrographic determination. Elution of Be and U with sulfosalicylic acid was carried out as follows: a) elution was only carried out to the appearance of the color of the uranium complex with sulfosalicylic acid (only Be eluted); in this case, 20 mg of the original uranium (free from beryllium) was added to a sample of eluate, and the residue analyzed spectrographically; b) the beryllium was eluted to a stage at which some of the uranium had come through. Observations were based on the color of the uranium complex; for elution of 20-40 mg of uranium, it was found sufficient to collect 25-40 ml of eluate with the clearly marked color of the uranium complex. The residue, after decomposing the complexes and calcining to U_3O_8, was analyzed spectrographically. The results are given in Table 2.

Accordingly, in order to obtain satisfactory results, it is necessary to elute 35-40 mg of uranium together with the beryllium. This suggests that the partition zones of Be and U even on the resin are, presumably, superimposed on each other, this being particularly the case during elution of traces of Be (down to 10^{-6}%).

Technique for determining traces of Be in uranium. A known amount of uranium, the amount depending on the expected beryllium content (1.5-2 g of uranium for a Be content down to 10^{-6}%), is dissolved in hydrochloric acid to which hydrogen peroxide has been added; the solution is evaporated almost to dryness and then diluted with water to 100 ml. The solution is acidified to 0.6 M with respect to HCl and is passed through a column 10 mm in diameter containing KU-2 resin in the H-form (15-20 g of resin in the air dry form for 1.5-2 g uranium). The rate at which the solution is passed through the column is 0.5 ml/min. The resin is then washed with 50 ml of water. and the Be eluted with sulfosalicylic acid (0.02-0.025 M) at a pH of 2.7-3. During this stage a clearly defined dark violet zone is observed which gradually passes down the column; the eluate prior to the elution of this ring, or before the eluate has a pH of 2.7-3, is discarded, and the following portion of eluate taken for analysis. Elution is complete when 35-40 ml of solution with the distinct color of the complex of uranium with sulfosalicylic acid has been collected (total volume of eluate 400-500 ml). The eluate is evaporated almost to dryness, 3-5 ml of concentrated H_2SO_4 is added to destroy the complexes and the residue is calcined, initially at 300-400° to burn off carbon, and then at 800-850° to obtain U_3O_8. The residue is weighed and the Be determined spectrographically. One determination takes about 40 hr.

SUMMARY

A combined method is suggested for the determination of down to 10^{-6}% of beryllium in uranium; the beryllium is concentrated chromatographically and then determined spectrographically. The experimental error is ± 20%.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION II. PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF URANIUM BY MEANS OF BROMOPYROGALLOL RED*

V. F. Luk'yanov and E. P. Duderova

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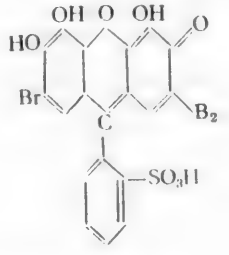
Bromopyrogallol red has been suggested as a complexonometric indicator for the determination of a number of elements [1]:



The reagent, which belongs to the sulfophthalein group of indicators, gives red solutions in acid media, and violet or blue colored solutions in neutral and alkaline media. It forms blue or blue-violet colored complexes with the following metal ions, at various pH values: Bi, Pb, Hg, Cu, Cd, Sb, Sn, Fe, Al, Ni, Co, Zn, Mn, Ca, Sr, Ba, Mg, rare earths, U, Th, Ti, Zr.

We have used bromopyrogallol red as a reagent for the uranyl ion. In the course of our work we established that the compound formed is stable at pH 5-7. A urotropine buffer solution with pH 6.5-7 was used to maintain the necessary pH. In this medium the reagent has a red color, while its complex with uranium has a blue-violet color.

The absorption curves of the reagent and the complex are shown in Fig. 1, while the calibration curve is shown in Fig. 2.

It is clear from Fig. 1 that the most suitable wavelength for the work is 620 mμ, at which the difference between the optical densities of the complex and the reagent is a maximum.

The complex is formed almost instantaneously, and its color is very stable (for at least 24 hr).

The maximum optical density of the solutions, obtained by the Ostromyslenskii-Job method, is observed at a ratio of UO_2^{2+} : reagent = 1 : 1 (at 600, 620 and 630 mμ) for three different initial molar concentrations of uranium salt and reagent (0.9×10^{-4} M; 1.8×10^{-4} M; and 3.6×10^{-4} M).

The molar extinction coefficient of solutions of the compound at 620 mμ is 8.8×10^3 (mean of three determinations).

*For Communication I, see Zhur. Anal. Khim. 15, 184 (1960).

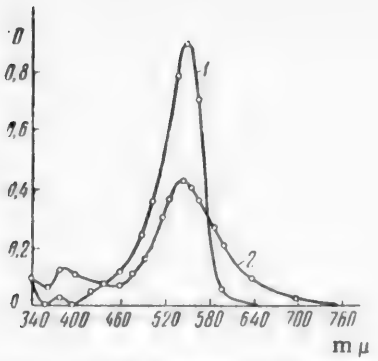


Fig. 1. Light absorption of solutions of the complex of uranium with bromopyrogallol red, and of the reagent (SF-4, cuvette 1 cm). 1) 2×10^{-5} M solution of pyrogallol red; 2) solution of the complex of uranium with bromopyrogallol red at a ratio of UO_2^{2+} : reagent = 1 : 1.

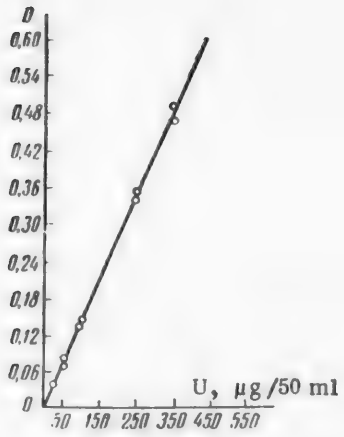


Fig. 2. Calibration for the determination of uranium with pyrogallol red (FÉK-M, red filter, cuvette 3 cm).

When an FÉK-M photocolorimeter is used, uranium can be reliably determined at a minimum concentration of 0.5 μg/ml (red filter, cuvette 3 cm, D = 0.04).

The most suitable concentration range for the photometric determination of uranium is 25 to 250 μg uranium in 50 ml; Beer's law is observed over this range.

Quantitative determination of uranium requires preliminary separation from accompanying elements, most of which form compounds with bromopyrogallol red [1]. We decided on a method developed by V. I. Titov, A. A. Lavrova, and E. P. Osiko in 1956. This method is based on separating uranium with α-nitroso-β-naphthol as a coprecipitant, in the presence of sodium ethylene diaminetetraacetate (EDTA-Na). When this separation method is used, appreciable amounts of iron and traces of certain other metals are precipitated together with the uranium. We used EDTA-Na for eliminating interference from iron; the former was added (in slight excess) until no color of iron thiocyanate was detected.

Analytical procedure. One-half to 1 g of test material (depending on the uranium content) is decomposed with hydrochloric acid containing hydrogen peroxide by heating on a sand bath. The solution is diluted with water and the insoluble residue filtered off and washed. To the filtrate, whose volume should be about 100 ml, is added 15-17 ml of a 10% solution of EDTA-Na; the pH is adjusted to 7.5-8 using neutral red (or universal indicator), and the solution is then heated to the boiling point. The pH, which thereby drops, is adjusted again by adding ammonia free from CO_2.

The uranium is precipitated in the hot solution with 10-13 ml of a 2% alcoholic solution of α-nitroso-β-naphthol. The solution plus precipitate are allowed to stand overnight. On the following day the precipitate is filtered off and carefully washed with cold water until completely colorless wash liquors are obtained. The precipitate is dried, ashed, and calcined gently in a porcelain crucible at 550°. The residue is dissolved in the crucible in a few ml of concentrated hydrochloric acid; the solution is evaporated to a few drops, and the contents of the crucible quantitatively transferred to a 50 ml standard flask. One to two drops of a 10% solution of ammonium thiocyanate is added, and 2% EDTA-Na solution added dropwise until the red color disappears; 10-20 drops of EDTA-Na is then added in excess. Five ml of a 25% solution of urotropine (pH 6, 5-7) is added, followed by 2 ml of a 0.1% solution of bromopyrogallol red in 50% alcohol. The volume of the solution is made up to the mark with twice-distilled water; the whole is carefully mixed, and the optical density is measured on an FÉK-M apparatus with a red filter, using a 3 cm cuvette. During construction of a calibration curve, 2 ml of the 2% solution of EDTA-Na is added to the uranium solutions.

We also used partition chromatography on silica gel [2] for separating uranium from interfering elements. To the test solutions, after removal of interfering elements and prior to the photometric determination, was added 2-5 drops of the 2% EDTA-Na solution. The appropriate amounts of EDTA-Na were also added to the solutions used for constructing the calibration curve.

Photometric Determination of Uranium in Standard Ores by Means of Bromopyrogallol Red

Sample No.	Specified uranium content, %	Separation method	Uranium found photometrically, %	Mean, %
9	0.070	Precipitation with α-nitroso-β-naphthol	0,071; 0,0675; 0,0670; 0,065; 0,067; 0,073; 0,0705; 0,0705; 0,0675	0.069
		Partition chromatography	0,071; 0,070; 0,073; 0,071; 0,070; 0,069; 0,071	0,070
7	0.059	Precipitation with α-nitroso-β-naphthol	0,062; 0,057; 0,065; 0,061; 0,061; 0,059; 0,062; 0,065; 0,055	0.061
		Partition chromatography	0,060; 0,0596; 0,0596; 0,0596; 0,059; 0,060; 0,060; 0,060; 0,0592	0.060
27	0.103	Precipitation with α-nitroso-β-naphthol	0,100; 0,0995; 0,104; 0,100; 0,104; 0,104;	0.102
		Partition chromatography	0,104 ;0,103; 0,104; 0,103; 0,103; 0,103; 0,106; 0,103; 0,102; 0,103	0.103
2	0.22	The same	0,20; 0,21; 0,22; 0,23; 0,21; 0,218; 0,22; 0,218; 0,216	0.215
4	0.072	Precipitation with α-nitroso-β-naphthol	0,073; 0.074; 0,073; 0,075; 0,075; 0,070; 0,070; 0,068	0.072
29	0.0725	The same	0,0775; 0,071; 0,070; 0,070; 0,0737; 0,0703; 0,068	0.072
30	0.22	" "	0,21; 0,218; 0,216; 0,222; 0,205; 0,218; 0,222; 0,21	0.215

The use of the partition chromatographic method of separation gave satisfactory results.

The results obtained during the analysis of standard ores are given in the table.

SUMMARY

A technique has been developed for the photometric determination of uranium in ores by means of bromopyrogallol red.

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AMPEROMETRIC TITRATION OF SEXIVALENT URANIUM WITH DIVALENT CHROMIUM SALTS

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Most titrimetric methods of determining uranium are based on its oxidation–reduction reactions [1-5]. In amperometric methods of determining uranium, use is made of its precipitation reaction with potassium ferrocyanide [6], or the oxidation reaction of quadrivalent uranium [7]; the experimental accuracy is not high.

Some strong reducing agents (Cr^{2+}, Ti^{3+} [1, 8, 10] reduce sexivalent uranium to the quadrivalent state. We have studied the possibility of titrating sexivalent uranium amperometrically with solutions of divalent chromium salts, which are comparatively readily prepared, and which under certain storage conditions do not change their titer for a long time.

It has been established [11] that divalent chromium ions are oxidized on a rotating platinum microelectrode; the diffusion current at potentials of 0.3-1.1 v* is proportional to the concentration of divalent chromium ions.

The work was carried out on a VP-5 visual type polarograph made by "Geopribortsvetmet." The current was measured with an M-21 mirror galvanometer with a maximum sensitivity of 2.4×10^{-9} a/mm/m.

The rotating platinum microelectrode was prepared from a platinum wire (d = 0.5 mm, l = 5 mm), which was fused into a glass tube with a mercury contact. The electrode was rotated by an electric motor at the rate of 600 rpm. The reference electrode was a saturated calomel electrode connected to the electrolyzer via an agar-agar bridge.

A vibrating microelectrode [12] was used for titrating in small volumes (1-2 ml). Oxygen was removed from the solution by means of nitrogen which had been carefully purified from oxygen [13].

The divalent chromium salt solutions were prepared by a method suggested by Busev [14], using amalgamated zinc as the reducing agent. The $CrCl_2$ and $CrSO_4$ solutions prepared were standardized amperometrically against potassium dichromate [11]. The titer of the solutions did not change over a period of 25-30 days. 0.04195 N $CrCl_2$ and 0.04771 N $CrSO_4$ solutions were used in the work. Uranyl sulfate solution was prepared from the solid salt containing 53.03% U. The solution was acidified with sulfuric acid to a pH of 2.9. The uranium content of the solution was established gravimetrically (ammonia and hydroxyquinoline). The solution contained 12.35 mg U/ml.

The behavior of uranium compounds on a dropping mercury electrode has been studied [1]; the behavior of uranium on a rotating platinum microelectrode, however, has only been studied to a small extent. Rozental' and Veselovskii [15] have pointed out the complexity of the electrochemical oxidation of quadrivalent uranium compounds to the sexivalent state.

*Relative to the saturated calomel electrode.

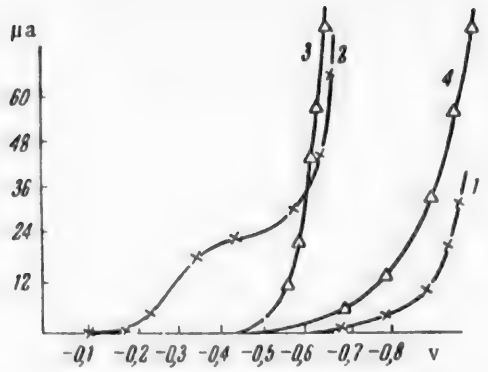

Fig. 1. Reduction of sexivalent uranium on a platinum microelectrode. 1) In a supporting electrolyte of 0.5 N K_2SO_4; 2) U^{VI} in a supporting electrolyte of 0.5 N K_2SO_4; 3) U^{VI} in a supporting electrolyte of an acetate buffer at pH 3.9; 4) in a supporting electrolyte of 0.5 N $(NH_4)_2CO_3$.

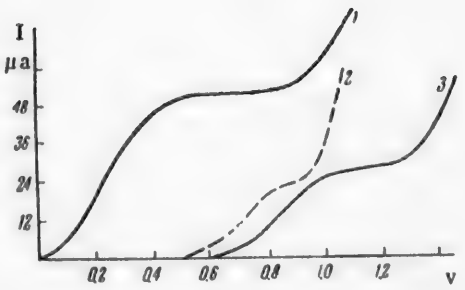

Fig. 2. Oxidation of quadrivalent uranium. 1) U^{IV} in a supporting electrolyte of acetate buffer, pH 3.9; 2) in a supporting electrolyte of 1 N HCl; 3) U^{IV} in a supporting electrolyte of 1 N H_2SO_4.

Reduction of sexivalent uranium on a platinum electrode was carried out in a supporting electrolyte of 0.5 N K_2SO_4; an acetate buffer, pH 3.9; and 0.5 N $(NH_4)_2CO_3$ in a N_2 atmosphere. The volt–ampere curves obtained (Fig. 1) show that the most suitable supporting electrolyte for the reduction of sexivalent uranium is 0.5 N K_2SO_4. Use of the cathodic reduction current of sexivalent uranium during amperometric determinations is strongly limited by the need for strict observance of the composition of the supporting electrolyte.

Quadrivalent uranium compounds were prepared by reduction of uranyl sulfate solution in a cadmium reducer or with $CrCl_2$, the amount of the latter added being such that 60-70% of the uranium was subjected to reduction.

The volt–ampere curves obtained are shown in Fig. 2. Increasing the acidity of the supporting electrolyte shifts the oxidation wave of quadrivalent uranium toward more positive potentials. A proportionality between the value of the diffusion current and the uranium concentration of the solution is only observed when a buffer solution with a pH of 3.9 is used as a supporting electrolyte.

In carrying out amperometric determinations of sexivalent uranium based on reduction of uranium to its quadrivalent state, it is necessary to take into account the possibility of some distortion of the titration curve as a result of the oxidation of the quadrivalent uranium on the electrode when the electrode potential is sufficient for this process to occur.

The reduction of sexivalent uranium by divalent chromium salts has been used earlier for the potentiometric determination of microamounts of uranium, the titration being carried out at 70-80° [9, 10].

Our experiments showed that the reaction between sexivalent uranium and divalent chromium proceeds rapidly enough at room temperature, since the equilibrium values of the diffusion current are established fairly rapidly.

In carrying out amperometric titration a stream of nitrogen was passed through 15 ml of test solution, via a tube with a capillary tip (fine droplets of inert gas expel dissolved oxygen more rapidly) for 20-30 min. Titration was carried out at a potential of ± 0.6 v. As a result of a series of experiments it was established that acid concentration has considerable influence on the experimental accuracy of the determination of sexivalent uranium by means of divalent chromium salts.

When titrations are carried out in a supporting electrolyte of 1-6 N hydrochloric acid, the titration curves have an unusual shape (Fig. 3); initially, an increase in current is observed. Nevertheless, as can be seen from the results given in Table 1, results for the determination of uranium in a supporting electrolyte of 2-5 N HCl are completely satisfactory.

TABLE 1

Titration of Sexivalent Uranium with $CrCl_2$ Solution in a Supporting Electrolyte of HCl

HCl supporting electrolyte, N	U, mg		Error	
	taken	found	mg	%
1	6,16	6,10	—0,06	—1
2	6,16	6,15	—0,01	—0,3
3	6,16	6,15	—0,01	—0,3
4	6,16	6,15	—0,01	—0,3
4	3,36	3,36	0	0

TABLE 2

Titration of Sexivalent Uranium with $CrSO_4$ Solution in a Supporting Electrolyte of H_2SO_4

H_2SO_4 supporting electrolyte, N	U, mg		Error	
	taken	found	mg	%
1	1,30	1,19	—0,11	—8,5
2	3,08	3,07	—0,01	—0,3
2	1,25	1,25	0	0
4	6,04	6,02	—0,02	—0,3
4	5,14	3,17	0,03	0,9
4	3,14	3,13	—0,01	—0,3
6	6,55	6,54	—0,01	—0,2
8	6,17	6,42	0,25	4
4	0,673	0,674	0,001	0,01
4	0,673	0,675	0,002	0,3
4	0,337	0,340	0,003	0,7
4	0,337	0,337	0	0

TABLE 3

Determination of Sexivalent Uranium in the Presence of Pb^{2+}, Zr, and Th in a Supporting Electrolyte of 4 N HCl and 4 N H_2SO_4

Taken, mg				Ratio, element : U	U found, mg	Error	
Pb	Zr	Th	U			mg	%
12	—	—	6,04	1 : 2	6,03	—0,01	—0,1
60	—	—	6,29	1 : 10	6,30	0,01	0,1
50	—	—	1,12	1 : 50	1,13	0,01	0,9
—	300	—	6,05	1 : 50	6,03	—0,03	—0,5
—	230	—	2,36	1 : 100	2,37	0,01	0,5
—	1200	—	1,23	1 : 1000	1,23	0	0
	—	300	6,16	1 : 50	6,17	0,01	0,1
		500	1,22	1 : 500	1,23	0,01	0,4
		1000	1,22	1 : 1000	1,24	0,02	0,5

TABLE 4

Determination of Sexivalent Uranium and Trivalent Iron in Each Other's Presence in a Supporting Electrolyte of 4 N H_2SO_4

Ratio U : Fe	U, mg		Error, mg	Fe, mg		Error, mg
	taken	found		taken	found	
1 : 1,3*	2,10	2,15	0,05	2,74	2,70	0,04
1 : 1,3	2,10	2,13	0,03	2,69	2,66	—0,03
1 : 5*	2,47	2,47	0	12,04	12,05	0,01
1 : 5	2,47	2,48	0,01	12,04	12,07	0,03
1 : 10	2,47	2,40	—0,07	24,08	24,41	—3
1 : 10	2,47	2,43	—0,04	24,08	24,32	0,24
1 : 50	0,673	0,675	0,02	33,5	33,0	0,5

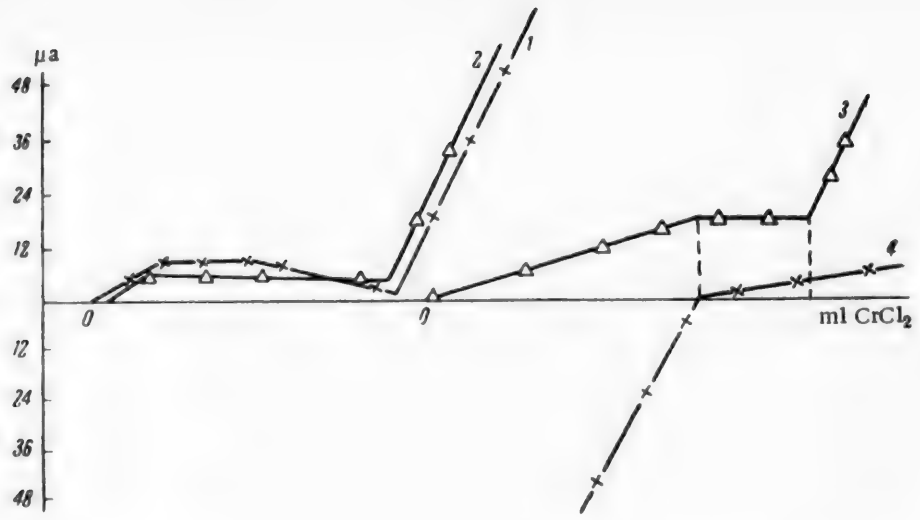

Fig. 3. Titration curves of sexivalent uranium and trivalent iron with divalent chromium salts. 1) U^{VI} in a supporting electrolyte of 4 N HCl, E = 0.5 v; 2) U^{VI} in a supporting electrolyte of 4 N H_2SO_4, E = 0.5 v; 3) U^{VI} and Fe^{III} in each other's presence in a supporting electrolyte of 4 N H_2SO_4; 4) Fe^{III} in a mixture with U^{VI}, E = 0 v.

When the titrations are carried out in a supporting electrolyte of sulfuric acid, the titration curves have the usual shape (Fig. 3), although at the start of the titration there is some increase in the current. During the determination of small amounts of uranium (0.6-0.3 mg), the titration was carried out in a volume of 1.5 ml in a special electrolyzer using a vibrating platinum microelectrode.

The titration results are given in Table 2.

Completely satisfactory results are obtained when the titration is carried out in a supporting electrolyte of 2-6 N H_2SO_4. By decreasing the volume of the solution being titrated during the determination of small amounts of uranium, it is possible to determine tenths of a milligram with satisfactory accuracy.

Results for the determination of uranium in the presence of lead are completely satisfactory right up to ratios of U : Pb = 1 : 50; on increasing the lead concentration further, precipitates of $PbCl_2$ and $PbSO_4$ separate out.

Satisfactory results were obtained for ratios of U : Zr and U : Th = 1 : 1000 (mean error ± 0.3%). Results for the determination of uranium in the presence of these elements are given in Table 3. The titration curves obtained during these determinations have the same shape as those obtained during titration of pure uranyl salts.

The main difficulty in developing a method for the amperometric determination of sexivalent uranium in the presence of trivalent iron was the reduction of the latter to the divalent state prior to the start of the reduction of sexivalent uranium.

During the determination of sexivalent uranium and trivalent iron in each other's presence, iron was first titrated with $CrCl_2$ solution at 0 v, while in another aliquot of the solution the sum of the two elements was titrated at a potential of 0.5 v (Fig. 3). The uranium content was found by difference. Satisfactory results were obtained up to a ratio of U : Fe = 1 : 50.

At ratios of U : Fe up to 1 : 10 it was found possible to determine both elements from one titration curve, since on carrying out titration at a potential of 0.5 v the curve had two sharp breaks, the first corresponding accurately to completion of reduction of trivalent iron, the other corresponding to completion of reduction of quadrivalent uranium (Curve 3, Fig. 3).

The titration results are given in Table 4.

We should like to express our gratitude to I. P. Alimarin for his valuable advice in the course of the work described here.

SUMMARY

A method has been developed for the direct amperometric titration of sexivalent uranium in pure solutions with a solution of a divalent chromium salt, using rotating and vibrating platinum microelectrodes. Lead at ratios up to U : Pb = 1 : 50 and zirconium and thorium at ratios up to 1 : 1000 do not interfere with the determination. The method permits determination of uranium in solutions containing trivalent iron.

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A QUANTITATIVE METHOD FOR THE DETERMINATION OF URANIUM ON THE BASIS OF ITS LUMINESCENCE IN PHOSPHORIC ACID SOLUTIONS

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The method of determining small amounts of uranium on the basis of the luminescence of beads (or alloys) of sodium fluoride [1, 2], which is in widespread use at the moment, is connected with a number of difficulties of a practical nature: the beads or alloys have to be prepared in the loop of a platinum wire or on platinum targets at a high temperature (about 1000°); when such a technique is used the intensity of the luminescence of the bead obtained depends on many factors (temperatures and duration of fusion, the atmosphere during calcining, and the cooling conditions). A quantitative method of determining uranium on the basis of its luminescence in aqueous solution would enable all these drawbacks to be overcome. Melkov and Sverdlov [3] have drawn attention to the fact that many nonluminescent uranium-containing minerals can be converted into a luminescent state by treating their surfaces with various reagents (phosphoric, sulfuric, and other acids); when this is done, uranium compounds are obtained which luminesce predominantly on excitation with short wave ultraviolet light.

In 1947 Levshin and co-workers, and later Novak [4], used the luminescence of uranium in sulfuric acid solutions for analytical purposes. A number of research workers [1, 5] have been occupied with the study of the possibility of testing ores for uranium on the basis of its luminescence in phosphoric acid solutions. Of particular interest in this connection is the work of Sill and Peterson [5].

The aim of the work described here was to develop a quantitative method of determining uranium on the basis of its fluorescence in phosphoric acid solutions, which have a number of advantages over sulfuric acid solutions; the luminescence intensity of sexivalent uranium in phosphoric acid solutions is significantly higher than that in sulfuric acid solutions; phosphoric acid itself does not luminesce on illuminating it with ultraviolet light, while sulfuric acid often luminesces as the result of the presence of organic materials (the luminescence is blue in color); in addition, phosphoric absorbs ultraviolet light to a smaller extent than other acids.

Properties of the luminescence of sexivalent uranium in phosphate solutions. We made a study of the relation between the luminescence intensity of uranyl nitrate solutions (concentration 100 μgU/ml) and the addition of a number of materials (Table 1). Measurements were made on a horizontal Pulfrich photometer, the solution being illuminated from above during excitation with ultraviolet light (253.7 mμ). A BUV-15 bactericide lamp fitted with a UFS-1 filter (for which it is convenient to use a Brumberg UB-1 ultrachemiscope [6]) served as the excitation source. A cuvette in which the distance between the working edges was 5 cm was used.

It is clear from Table 1 that phosphoric acid solutions of uranyl exhibit the highest luminescence intensity; the next in order are solutions containing unisubstituted phosphate, sulfate, and fluoride ions.

We should point out that the luminescence of sexivalent uranium in aqueous solutions is very sensitive to additions of various organic materials (glycerol, ethanol), reducing agents (hydrazine, hydroxylamine), and also to oxidizing agents (hydrogen peroxide), in the presence of which the luminescence intensity drops.

TABLE 1

The Relation between the Luminescence Intensity of Sexivalent Uranium and the Chemical Composition of the Solution

Material added	Amt. of additive, calculated in terms of the anion	Luminescence intensity in relative units
Na_2CO_3	5%	Very weak luminescence
$NaHCO_3$	5%	The same
NaCl	5%	" "
NaI	5%	No luminescence (the solution is yellow)
NaF	Saturated solution	22 (bright luminescence)
$NaHF_2$	" "	20 The same
Na_2SO_4	5%	33 " "
$NaHSO_4 \cdot 2H_2O$	5%	33 " "
$NaH_2PO_4 \cdot 2H_2O$	5%	36 " "
$Na_2HPO_4 \cdot 7H_2O$	5%	6 (weak luminescence)
$Na_3PO_4 \cdot 12H_2O$	5%	2 The same
Sodium acetate	5%	3 " "
Sodium oxalate	5%	No luminescence
Sodium citrate (tri-substituted)	5%	The same
Sodium tartrate (di-substituted	5%	" "
H_3PO_4	5%	100 (bright luminescence)
Sodium arsenite	5%	No luminescence

In Fig. 1 is shown the relation between the logarithm of the luminescence intensity (in relative units) and the concentration of sexivalent uranium in a 5% phosphoric acid solution. It follows from the results obtained that at very low concentrations (down to about 1×10^{-4} g U/ml) there is a linear relation between the luminescence intensity and concentration; on increasing the concentration further, the curve passes through a maximum which is found at about 2.5×10^{-4} g U/ml. Thus, sexivalent uranium can be quantitatively determined on the basis of its luminescence in aqueous phosphoric acid solutions from very low concentrations to about 1×10^{-4} g U/ml.

We tried to explain the increase in the luminescence intensity of sexivalent uranium in phosphoric acid solutions by a change in absorption. On adding phosphoric acid to a nitric solution of uranyl there is observed an increase in absorption (Fig. 2 , where curve 1 corresponds to the absorption of a solution whose uranium concentration is 1 μg/ml, while curve 2 corresponds to the absorption of the same solution, but, containing in addition, another 5% of phosphoric acid). Absorption was measured by means of an SF-4 spectrophotometer in the short wave side of the ultraviolet.

It follows from the results obtained that on addition of phosphoric acid to a nitric acid solution of sexivalent uranium, although there is an increase in absorption, nevertheless the luminescence intensity increases many times more in this case.

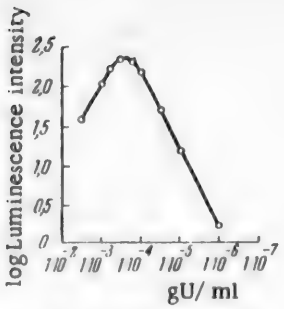

Fig. 1. Relation between luminescence intensity and uranium concentration in a 5% H_3PO_4 solution.

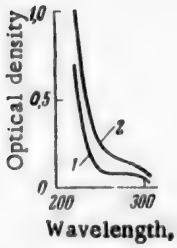

Fig. 2. Absorption curves of U^{VI} in solutions of HNO_3 (1) and a mixture of HNO_3 and H_3PO_4 (2).

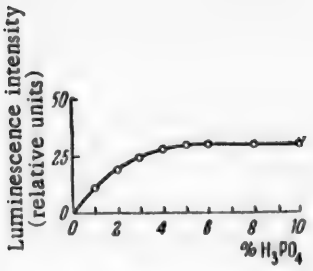

Fig. 3. Relation between the luminescence intensity of uranium in solution and H_3PO_4 concentration.

The luminescence of phosphoric solutions of uranyl is excited by both short wave and long wave ultraviolet light; nevertheless, in the case of dilute solutions (concentration less than 10 μg U/ml) excitation by the short wave ultraviolet (253.7 mμ) gives a considerably higher luminescence intensity. On exciting the luminescence with light from the BUV-15 lamp fitted with a UFS-1 filter it is possible to detect tenths of a gamma of U per ml, while when excitation is effected with a wavelength of 365 mμ the minimum uranium concentration that can be detected is two orders greater (PRK-4 lamp, UFS-3 filter).

One must make the special reservation that in the case of quantitative determination of uranium on the basis of its luminescence in aqueous solutions, the vessels (cuvettes) used should not luminesce when they are illuminated by ultraviolet light. Quartz vessels and vessels made from "pyrex" satisfy these requirements. The luminescence intensity of phosphoric solutions with low uranium contents (from a few tenths of a gamma to 10 μg U/ml) can also be measured by means of the EF-3 photoelectric luminescence photometer, which is produced by the Control-Measuring Apparatus factory of the Ministry of the Food Industry (Moscow), in which the primary filter is the UFS-1 filter and the secondary filter is the filter used for Vitamin B_1 determinations. Measurements are made in a quartz tube with a diameter of about 1.5 cm, the position of the latter being strictly fixed.

The luminescence intensity of sexivalent uranium in phosphoric acid solutions increases with decreasing temperature (the studies were made over the range 0 to 90°). In this connection, during quantitative determinations, the standard and test solutions should have the same temperature, e.g., + 20°.

It should also be pointed out that the luminescence intensity of sexivalent uranium in phosphoric acid solutions depends, over a certain range, on the phosphoric acid concentration, as is evident from Fig. 3, in which the phosphoric acid concentration (in percent) is plotted along the abscissa, while the luminescence intensity (in relative units) is plotted on the ordinate; the uranium concentration in solution is 3 μg U/ml.

From Fig. 3 it is clear that on increasing the phosphoric acid concentration to 5% the luminescence intensity of uranium in the solution increases to reach a definite value, which remains constant on increasing the phosphoric acid concentration further.

In the method suggested below, 5% phosphoric acid solutions are recommended.

On adding most of the foreign ions to phosphoric acid solutions of uranyl, the luminescence intensity usually drops. Data on the effect of impurities on the luminescence of uranium are given in the paper by Sill and Peterson [5]. The quenching effect of impurities is more clearly expressed in aqueous solutions than is the case for the determination of uranium on the basis of the luminescence of beads or alloys prepared on a sodium fluoride base. Quantitative determination of uranium on the basis of its luminescence in aqueous phosphate solutions is possible, when the impurities which act as quenching agents are removed (Fe, Cu, Mn, Cr, Ni, Co, etc.).

Separation of uranium from quenching impurities. We used an extraction method for this purpose. The extractant used was tributyl phosphate, which possesses a high selectivity [7, 8], while the diluent was carbon tetrachloride, and calcium nitrate was used as a salting out agent. Quenching impurities were first complexed by addition of sodium ethylenediaminetetraacetate (EDTA-Na). After the uranium had been extracted from the organic phase, it was re-extracted into the aqueous phase and was then determined on the basis of its luminescence in phosphate solutions.

TABLE 2

Limiting Permissible Ratios of Quenching Impurities to Uranium in the Original Solutions

Elements	Composition of the added material	Limiting-permissible ratio of quenching impurity to uranium	
		using EDTA-Na	without addition of EDTA-Na
Fe^{III}	$Fe(NO_3)_3 \cdot 9H_2O$	2500	200
Cr^{VI}	$K_2Cr_2O_7$	100	100
Cr^{III}	$Cr(NO_3)_3 \cdot 9H_2O$	100	100
Ni^{II}	$Ni(NO_3)_2 \cdot 6H_2O$	7500	45
Cu^{II}	$Cu(NO_3)_2 \cdot 6H_2O$	80 000	60
Rare earths	Nitrates	—	250
Th^{IV}	$Th(NO_3)_4 \cdot 4H_2O$	4500	90
Ce^{IV}	$Ce(OH)(NO_3)_3 \cdot 3H_2O$	—	200
Zr^{IV}	$Zr(NO_3)_4 \cdot 5H_2O$	8500	450
Mo^{VI}	$(NH_4)_2MoO_4$	200	500
V^{V}	NH_4VO_3	12 000	400
W^{VI}	$Na_2WO_4 \cdot 2H_2O$	5000	1200
As^{V}	$Na_3AsO_4 \cdot 12H_2O$	2000	2000

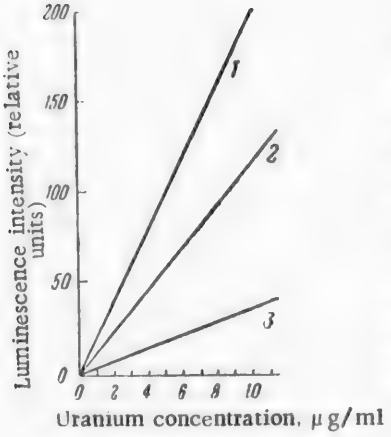

Fig. 4. The relation between the intensity of U^{VI} in solution and the presence of tributyl phosphate and CCl_4. 1) Solutions of U^{VI} in 5% H_3PO_4; 2) re-extract (5% H_3PO_4 after boiling; 3) re-extract (5% H_3PO_4) without boiling.

The reagents used should not luminesce on being illuminated with ultraviolet light, nor should they quench the uranium luminescence.

The use of "pure" grade tributyl phosphate for extracting the uranium leads to lower results when the latter is determined on the basis of its luminescence in the aqueous re-extracts than when purified tributyl phosphate is used; accordingly, the tributyl phosphate was purified. To 100 ml of the commercial tributyl phosphate was added 400 ml of carbon tetrachloride and 750 ml of 1% NaOH solution. The mixture was vigorously shaken, and, after it had separated into two layers, the organic phase was separated; the latter was then washed twice with 750 ml lots of water. To the washed residue was added 5 g of activated charcoal powder ("clarifying" grade), and, after vigorous shaking the residue was passed through folded filter paper. The filtered solution of tributyl phosphate in carbon tetrachloride was washed twice with 750 ml of water, and again filtered through folded filter paper.

Aqueous solutions of EDTA-Na prepared by dissolving varying amounts of the commercial preparation sometimes exhibited an intense blue fluorescence on being illuminated with ultraviolet light, and only EDTA-Na which had been purified by a published method [9], was found to be satisfactory. 0.25-0.5 g of EDTA-Na (depending on the amount of interfering elements) was added to 25 ml of the test solution, the pH of which was adjusted to 2.5-3.0 (by means of HNO_3 or NaOH depending on the reaction of the solution). Under these conditions, elements which, though they are only extracted to a negligible extent by tributyl phosphate from aqueous solution of calcium nitrate, are strong quenchers (iron, copper, etc) are masked by EDTA-Na and remain in the aqueous phase. As a result of this it becomes possible to determine very small amounts of uranium (less than 1 μg U/ml) in solutions containing large amounts of impurities.

Extraction of uranium with an equal volume of a 20% solution of tributyl phosphate in carbon tetrachloride from nitric acid solutions containing 40% $Ca(NO_3)_2 \cdot 4H_2O$ ensures a high percentage extraction of uranium (about 99.9%). Extraction under the same conditions with two successive equal portions of tributyl phosphate in carbon tetrachloride makes it possible to extract uranium quantitatively.

Both pure water and phosphoric acid solutions (from 5 to 10%) proved suitable for re-extraction of the uranium from the organic phase into the aqueous phase.

Since during re-extraction of uranium with 5% phosphoric acid the aqueous phase dissolves the tributyl phosphate and carbon tetrachloride, the luminescence intensity of uranium in these solutions is less than that of phosphoric acid solutions of uranyl of the same concentration, but free from the impurities indicated. Boiling the re-extracts for not less than 2-3 min favors a significant increase in the luminescence intensity of uranium in solution; this is possibly the result of evaporating off the carbon tetrachloride. These regularities are seen in Fig. 4, where curve 1 corresponds to solutions of sexivalent uranium in 5% H_3PO_4, curve 2 corresponds to re-extracts boiled for 5 min, and curve 3 corresponds to re-extracts which had not been boiled beforehand.

Thus, during quantitative determination of uranium on the basis of the luminescence of its aqueous phosphoric acid solutions it is essential that the standard and test solutions be prepared under identical conditions: identical extraction, re-extraction, and subsequent boiling and cooling.

The permissible ratios of quenching impurities to uranium for which it is still possible to determine uranium quantitatively without resorting to the method of "known additions" were determined. These results are given in Table 2; these results were obtained with and without EDTA-Na.

The following experimental procedure was adopted for establishing these ratios. A series of aqueous solutions was prepared containing 40% calcium nitrate, 1 μg U/ml (in the form of uranyl nitrate), and various amounts of the quenching impurities whose influence it was desired to examine. The nitric acid concentration of the solutions was 0.2 M. The method of adding EDTA-Na has been indicated above. To 25 ml of each solution contained in a separating funnel was added 12.5 ml of a 20% solution of tributyl phosphate in carbon tetrachloride; the mixture was vigorously shaken for 2 min and after separation into two layers the organic phase was filtered through dry filter paper. To the aqueous phase remaining in the separating funnel was added another 12.5 ml of the solution of tributyl phosphate in carbon tetrachloride, and the extraction repeated. Both fractions of the extract were transferred to a separating funnel, and 12.5 ml of a 5% phosphoric acid solution added and the whole shaken vigorously for 2 min. After separating into two layers, the lower organic phase was run into another similar funnel, while the aqueous phase remaining was poured into a 60-75 ml quartz beaker. To the organic phase was added another 12.5 ml of 5% phosphoric acid; the whole was shaken and left to separate into layers. This re-extract was combined with the fraction of re-extract obtained earlier and the combined re-extracts boiled for 10 min. After cooling, the solution was transferred to a 25 ml standard flask and diluted with water to the mark. The luminescence intensity of the solutions obtained was measured in relative units and these results were compared with the corresponding results obtained for a uranium solution free from the quenching element. The maximum content of quenching element which in the original test solution still did not lead to an appreciable change in the luminescence intensity of uranium in the re-extract (less than 2%) was accepted as the limiting permissible content.

The method which we have suggested for the determination of small amounts of uranium on the basis of its luminescence in phosphate solutions has been used for determining the uranium content (of the order of 1 μg U/ml and less) of synthetic solutions containing large amounts of quenching impurities (Fe, Cr, Cu, Ni, Co, etc.) as compared to the uranium. The results obtained are characterized by good reproducibility. The experimental accuracy for the determination of about 1 μg U/ml is + 10%. An analysis does not take longer than 25 min.

The authors wish to thank P. N. Palei for his valuable advice and interest.

SUMMARY

A highly sensitive method has been developed for the quantitative determination of uranium, which is based on the luminescence of the latter in phosphoric acid solutions. The method includes the preliminary removal of uranium from quenching impurities by complexing the latter with sodium ethylenediaminetetraacetate, extraction of the uranium with a solution of tributyl phosphate in carbon tetrachloride (salting out agent calcium nitrate), with subsequent re-extraction of the uranium into the aqueous phase by a phosphoric acid solution and determination of the uranium on the basis of its luminescence intensity in the re-extract obtained.

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THE USE OF SELENOUREA IN ANALYSIS

COMMUNICATION II. PHOTOMETRIC DETERMINATION OF RUTHENIUM AND OSMIUM BY MEANS OF SELENOUREA WITHOUT THEIR PRELIMINARY SEPARATION. THE COMPOSITION AND STABILITY OF THE SELENOUREA COMPLEX OF RUTHENIUM*

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Several photometric methods are known for the determination of ruthenium. The simplest of them, but the least selective, are methods based on measurement of the color of K_2RuCl_5 [1] and ruthenate in an alkaline medium [2]. During the determination of ruthenium by means of p-nitrosodimethylaniline [3] and 1,10-phenanthroline [4], ruthenium must be separated beforehand by distillation as RuO_4. Thiourea [5-9], dithiooxamide [10, 11], thiocyanate [12], and many derivatives of thiourea and thiosemicarbazide [13-15] have also been used for the photometric determination of ruthenium. In strongly hydrochloric acid media, on heating, these reagents form blue colored compounds with ruthenium [17].

Osmium also reacts with sulfur-containing reagents. The compounds of osmium with these reagents are characterized by a narrower absorption band, which is shifted toward the short wave part of the spectrum, while the analogous compounds of ruthenium possess a wider absorption band which is shifted toward the long wave part of the spectrum. Thus, ruthenium can be determined in the presence of osmium, but in order to determine osmium it is always necessary to separate ruthenium.

In the first communication [16] it was shown that selenourea, like thoiurea, reacts with many heavy metals to form colored compounds. Selenourea also forms soluble, colored complexes with ruthenium and osmium. The present article is devoted to results on the determination of the composition and stability of the selenourea complex of ruthenium, and a description is given of a selenourea method for the determination of ruthenium and osmium without their preliminary separation.

The effect of acidity on the formation of the selenourea complexes of ruthenium and osmium. In order to clarify the effect of acidity on the formation of the selenourea complexes of ruthenium and osmium, experiments were carried out as follows. To a constant volume of a solution of the metal salt was added a constant amount of a selenourea solution and various amounts of concentrated hydrochloric acid. The solutions were then diluted with 1 M hydrochloric acid to 10 ml, they were thoroughly mixed, and the optical density of the selenourea complex of ruthenium measured at 760 mμ, and that of osmium at 600 mμ, i.e., in the region of their maximum absorption (Fig. 1). From Fig. 2 it is clear that the optimum acidity for the formation of the selenourea complex of osmium is 1 N HCl, while that for ruthenium is 7 N HCl. A solution with an acidity as high as this is not convenient in practice; accordingly, ruthenium was determined at 6 N HCl.

*For Communication I, see Zhur. Anal. Khim. 13, 3 (1958).

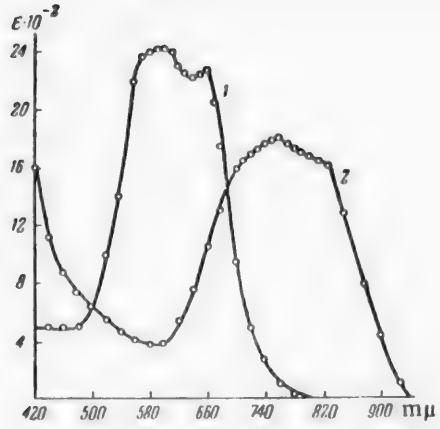

Fig. 1. The absorption curves of the selenourea complexes of osmium (curve 1) and ruthenium (curve 2). The selenourea concentration of the solutions is equal in both cases to 0.2 M.

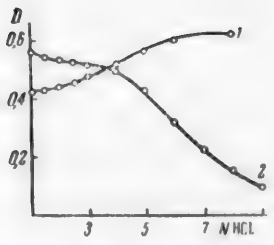

Fig. 2. The relation between the formation of the selenourea complexes of ruthenium (curve 1) and osmium (curve 2), and hydrochloric acid concentration. The concentrations of the reactants in the final volume were: osmium, 2.5×10^{-4} M; selenourea, $1 \times \times 10^{-1}$ M; ruthenium, 8×10^{-4}M; selenourea 1.5×10^{-1} M.

Thiourea speeds up the formation of the colored selenourea complex of osmium somewhat and stabilizes the selenourea complex of ruthenium. Because of this, for the determination of osmium and ruthenium urea was added to the test solution first, and selenourea then added.

The composition of the selenourea complex of ruthenium was determined by the isomolar series method [18]. It is clear from Fig. 1 that the composition of the compound is best studied in the spectral region 720-800 mμ; all the other components of the system do not absorb light in this spectral region.

Solutions (0.01 M) of ruthenium and selenourea were prepared in order to determine the composition of the complex. The hydrochloric acid concentration in both solutions was 1 N. These solutions were then mixed in various proportions and concentrated hydrochloric acid added so that its concentration in the final volume was 6 N; the total volume was kept constant. The optical density of the solutions was measured at 760 mμ on an SF-4 spectrophotometer. From Fig. 3 it is clear that the composition of the selenourea complex of ruthenium corresponds to a ratio of the reactants* of $[Ru^{4+}] : [Sem] = 1 : 3$.

The sharp break on the left hand side of the curve shows that the compound of ruthenium with a ratio of ruthenium and selenourea less than 1 : 2 does not exhibit light absorption in this region.

The stability of the selenourea complex of ruthenium. Formation of the selenourea complex of ruthenium can be represented by the scheme:

$$\underset{\text{colorless}}{Ru\ Sem_x^{4+}} + n\ Sem \rightleftharpoons \underset{\text{colored}}{Ru\ Sem_x^{4+}} + n \qquad (1)$$

The instability constant of the complex will be of the form:

$$K = \frac{[Ru\ Sem_x^{4+}]\,[Sem]^n}{[Ru\ Sem_{x+n}^{4+}]} \qquad (2)$$

The extent to which the ruthenium is bound in the colored compound depends on the selenourea concentration.

The numerical value of the instability constant of the selenourea complex of ruthenium was calculated in the same way as that of the selenourea complexes of bismuth [16]. For this purpose** solutions were prepared which

*$Se = C\begin{matrix}NH_2\\NH_2\end{matrix}$ will be denoted hereinafter by Sem.

**A solution of $RuOHCl_3$ prepared as described in [19] was used. It might be assumed that quadrivalent ruthenium is reduced by selenourea to trivalent ruthenium, which also forms a selenourea complex. Experiments showed, however,

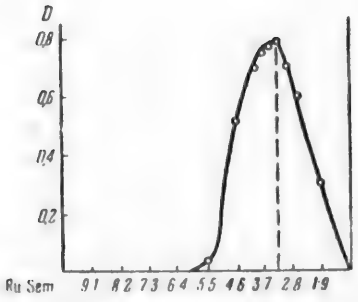

Fig. 3. Composition–optical density curve of the selenourea complex of ruthenium.

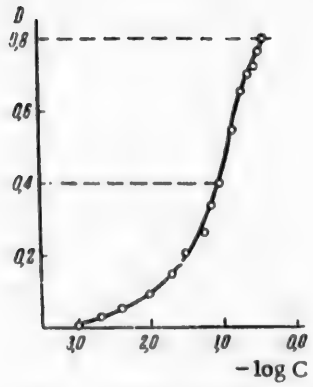

Fig. 4. Relation between the optical density of solutions of the selenourea complex of ruthenium and selenourea concentration.

TABLE 1

Formation of the Colored Selenourea Complex of Ruthenium as a Function of Excess Selenourea

$[Sem]_{total}$	$[Sem]_{excess}$	$-\log[Sem]_{excess}$	D	$[Ru\,Sem_{x+n}^{4+}]$	$-\log\frac{[Ru\,Sem_{x+n}^{4+}]}{[Ru_{total}^{4+}]-[RuSem_{x+n}^{4+}]}$
0,001	$9,9\cdot10^{-4}$	3,0	0,005	$0,03\cdot10^{-4}$	2,22
0,002	$1,98\cdot10^{-3}$	2,7	0,036	$0,22\cdot10^{-4}$	1,34
0,004	$3,89\cdot10^{-3}$	2,41	0,058	$0,36\cdot10^{-4}$	1,11
0,006	$5,87\cdot10^{-3}$	2,23	0,067	$0,42\cdot10^{-4}$	1,04
0,008	$7,86\cdot10^{-3}$	2,10	0,077	$0,48\cdot10^{-4}$	0,97
0,01	$9,84\cdot10^{-3}$	2,01	0,088	$0,55\cdot10^{-4}$	0,91
0,02	$1,97\cdot10^{-2}$	1,71	0,150	$0,94\cdot10^{-4}$	0,64
0,04	$3,96\cdot10^{-2}$	1,54	0,218	$1,36\cdot10^{-4}$	0,43
0,06	$5,94\cdot10^{-2}$	1,23	0,257	$1,60\cdot10^{-4}$	0,33
0,08	$7,94\cdot10^{-2}$	1,10	0,335	$2,10\cdot10^{-4}$	0,14
0,10	$9,92\cdot10^{-2}$	1,0	0,415	$2,60\cdot10^{-4}$	—0,03
0,15	$1,49\cdot10^{-1}$	0,83	0,550	$3,14\cdot10^{-4}$	—0,23
0,20	$1,99\cdot10^{-1}$	0,70	0,660	$4,12\cdot10^{-4}$	—0,67
0,25	$2,49\cdot10^{-1}$	0,60	0,700	$4,37\cdot10^{-4}$	—0,84
0,30	$2,99\cdot10^{-1}$	0,52	0,730	$4,56\cdot10^{-4}$	—1,02
0,35	$3,49\cdot10^{-1}$	0,46	0,770	$4,82\cdot10^{-4}$	—1,41
0,40	$3,98\cdot10^{-1}$	0,40	0,800	$5,0\cdot10^{-4}$	—
0,45	$4,43\cdot10^{-1}$	0,35	0,800	$5,0\cdot10^{-4}$	—

contained a constant amount of ruthenium equal to 5×10^{-4} M while the selenourea concentration was increased all the time; the optical density was measured at 760 mμ 30 min after pouring the solutions together. The acidity of the solutions was 6 N with respect to HCl in all cases. Water was used as the reference solution. The results obtained are given in Table 1 and in Fig. 4.

The concentration of the colored ruthenium complex was determined in the same way as the concentration of the colored bismuth complexes [16].

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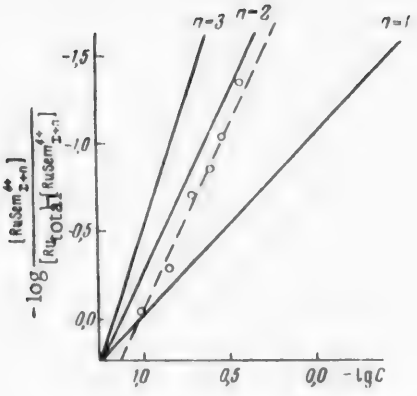
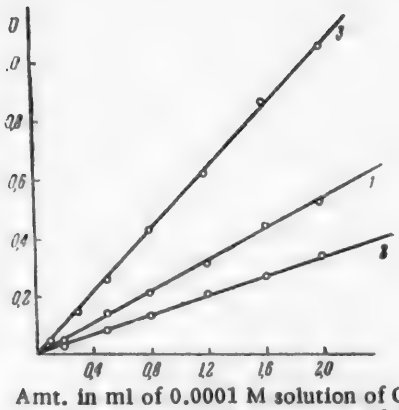
that $RuOHCl_3$ electrolytically reduced to $RuCl_3$ [19] only partially reacts with selenourea to form a colored reaction product. This apparently results from the presence of insignificant amounts of quadrivalent ruthenium in the chloride of trivalent ruthenium.



ig. 5. The effect of excess selenourea on the formation of the selenourea complex of ruthenium.



Amt. in ml of 0.0001 M solution of Os
Amt. in ml of 0.0035 M solution of Ru

Fig. 6. Calibration curves: for ruthenium at 760 mμ (curve 1) and at 600 mμ (curve 2); for osmium at 600 mμ (curve 3).

Reasoning in the same way, we get the following equation:

$$d\log\frac{[Ru\,Sem^{4+}_{x+n}]}{[Ru^{4+}_{total}]-[Ru\,Sem^{4+}_{x+n}]}:d\log[Sem] \qquad (3)$$

Equation (3) corresponds to that for a straight line. When the values of the ratio of the negative logarithms of the concentration of the complex to the concentration of free ruthenium which has not been converted into the colored compound are plotted on the same scale on the graph, the slope of the straight line corresponds to n.

As can be seen from Fig. 5, formation of the colored selenourea complex of ruthenium depends on the square of the selenourea concentration.

Taking into account all that has been said above, the equation for the formation of the colored selenourea complex of ruthenium can be depicted as follows:

$$\underset{\text{colorless}}{RuSem^{4+}} + 2\,Sem \rightleftarrows \underset{\text{colored}}{RuSem_3^{4+}}, \qquad (4)$$

from which

$$K_{RuSem_3^{4+}} = \frac{[RuSem^{4+}]\,[Sem]^2}{[RuSem_3^{4+}]} \qquad (5)$$

When half of the ruthenium has been bound as the colored compound, the numerical value of the instability constant is equal to the square of the excess selenourea concentration. The excess selenourea concentration is found from the curve in Fig. 4. The optical density corresponding to the complexing of half the ruthenium into a colored complex will be

$$\frac{0.800}{2} = 0.400.$$

Such a value for the optical density corresponds to a concentration of excess selenourea of 10^{-1} M, while an approximate numerical value of the instability constant of the complex will be equal to:

$$K_{RuSem_3^{4+}} = \frac{[RuSem^{4+}]\,[Sem]^2}{[RuSem_3^{4+}]} = (10^{-1})^2 = 10^{-2}$$

The value of the instability constant of the selenourea complex of ruthenium shows that the selenourea complex of ruthenium dissociates to a considerably greater extent than the thiourea complex of ruthenium [20]. All the same, selenourea has an advantage over thiourea in that it permits simultaneous determination of ruthenium and osmium without their separation.

TABLE 2

Results for the Determination of Ruthenium and Osmium by Means of Selenourea

Ru taken, μg	Ru found, μg	Error, %	Os taken, μg	Os found, μg	Error, %
353;5	353,5	0	190,0	190,0	0
35,35	35,35	0	380,4	374,3	—1,5
530,0	512,57	—3,3	380,4	376,2	—1,0
777,7	798,91	2,7	285,3	91,0	2,0
176,75	169,68	- 4,0	0,0	0,0	0

Determination of ruthenium and osmium by means of selenourea without their preliminary separation. It is clear from Fig. 1 that the selenourea complex of osmium exhibits maximum light absorption at 600 mμ while the selenourea complex of ruthenium only absorbs light weakly at this wavelength. The selenourea complex of ruthenium exhibits maximum light absorption at 760 mμ while the osmium complex does not absorb at this wavelength. The method of determining ruthenium and osmium in eachother's presence is based on measuring the optical density of the selenourea complex of ruthenium at 760 mμ in a strong hydrochloric acid solution. Subsequently, in 1 N hydrochloric acid, at 600 mμ, the total optical density of the selenourea complexes of ruthenium and osmium is measured; knowing the ruthenium content, the optical density corresponding to ruthenium at 600 mμ is subtracted from the total optical density and the osmium content found.

Urea was added to stabilize the selenourea complex of ruthenium and to accelerate the formation of the selenourea complex of osmium.

Experimental procedure. To 2.5 ml of the test solution which is 1 N with respect to hydrochloric acid is added 4.5 ml of concentrated hydrochloric acid (the hydrochloric acid concentration in the final volume should be about 6 N) followed by 1 ml of 5 M urea solution and 2.0 ml of 0.5 M selenourea solution. Half an hour after preparing the solutions, the optical density is measured at 760 mμ. The colored solutions are stable for 45 min, after this period the solutions become turbid and the optical density increases. The ruthenium content is found by means of a calibration curve constructed beforehand.

In order to determine osmium, to 2.5 ml of the test solution which is 1 N with respect to hydrochloric acid is added 0.5 ml of 5 M urea solution and 2 ml of 0.5 M selenourea in 1 N HCl. The color intensity is measured at 600 mμ half an hour after preparing the solution. Knowing the ruthenium content, the optical density found by means of the calibration curve for the given amount of ruthenium at 600 mμ is subtracted and the osmium content found by the calibration curve.

The calibration curves are shown in Fig. 6.

In Table 2 are given some results obtained during the determination of ruthenium and osmium in synthetic mixtures by this method.

It is clear from this table that the experimental errors for the determination of ruthenium and osmium are quite permissible.

Determination of ruthenium and osmium takes 45-60 min. The method permits determination of 2 to 60 μg Ru/ml and from 2 to 60 μg Os/ml.

The other platinum metals, with the exception of very large amounts of palladium, do not interfere.

SUMMARY

The composition and stability of the selenourea complex of ruthenium have been studied. It has been established that selenourea forms with ruthenium a colored compound which exhibits maximum light absorption at 760 mμ; the ratio of the components in this compound $[Ri^{4+}] : [Sem] = 1 : 3$.

The stability of the selenourea complex of ruthenium is characterized by the following approximate numerical value of its instability constant:

$$K_{RuSem_3^{4+}} = \frac{[RuSem^{4+}]\,[Sem]^2}{[RuSem_3^{4+}]} = 10^{-2}$$

A method has been developed for the determination of ruthenium and osmium without their preliminary separation. Using this method it is possible to determine from 2 to 60 μg Ru/ml and the same amounts of osmium in the presence of the platinum metals, apart from very large amounts of palladium.

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PHOTOMETRIC DETERMINATION OF NITROGEN IN TITANIUM CARBIDE AND BORIDE AND IN OTHER REFRACTORY MATERIALS

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Most of the methods in current use for determination of nitrogen include its lengthy separation from the other components of the test sample by distilling it off as ammonia from an alkaline solution. It is considerably more convenient to use phenol and its homologs and hypochlorite or hypobromite. This reaction has been used mainly for the determination of ammonia in water [1-3]. Lapin and Gein [4] replaced phenol by thymol and hypochlorite by hypobromite. The colored compound formed in this case is extracted with organic solvents; the color of the aqueous layer and possible separation of precipitates in the aqueous layer do not interfere, according to the observations of these authors. The overwhelming majority of cations and anions do not interfere with nitrogen determination [5]; thus the method has a high selectivity. Veinberg [6, 7] has used the thymol-hypobromite reaction for ammonia for the determination of nitrogen in steels. Nevertheless, he has not indicated what the acidity of the solution should be in order to carry out the reaction for ammonia, so that it is not possible to reproduce his technique.

The aim of the work described here was to study the conditions for carrying out the thymol-hypobromite reaction for ammonia and its application to the determination of nitrogen in titanium carbide and other refractory materials.

EXPERIMENTAL METHOD

1. Extraction of the dye formed as a result of the thymol-hypobromite reaction for ammonia with various organic solvents. Diethyl and diisopropyl ether are normally recommended for the extraction [5, 7].

We examined the solubility of the dye formed in various organic solvents. The following results were obtained:

a) Carbon tetrachloride, chloroform, dichloroethane, benzene, toluene, and o-xylene extract the dye from the aqueous layer to form pale orange colored solutions. Separation into layers proceeds readily.

b) Diethyl ether, isoamyl acetate, and diisopropyl ether extract the dye to form bright rose colored solutions. Separation into layers occurs readily, except in the case of diisopropyl ether.

c) n-Butanol and isoamyl alcohol extract the dye from aqueous solutions to give emerald green colored solutions. Separation proceeds readily. On adding the water-soluble alcohols ethanol, methanol, and glycerol to the opaque alkaline aqueous solution of the dye, which is blue in color, the solution acquires an emerald green color and becomes transparent.

These experiments showed, therefore, that brightly colored extracts are obtained on using ethers and alcohols. Of the ethers and esters tested, we settled on isoamyl acetate, which has a lower volatility and on using which the layers separate readily while of the alcohols we chose n-butanol, since the color of the layer obtained with n-butanol, for the same nitrogen content, is brighter than that obtained with isoamyl alcohol.

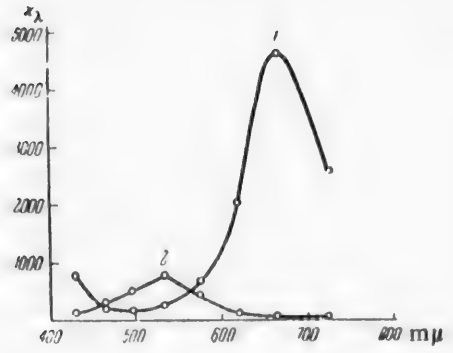

Fig. 1. Absorption curves of extracts of thymolindophenol in n-butanol (1) and in isoamyl acetate (2).

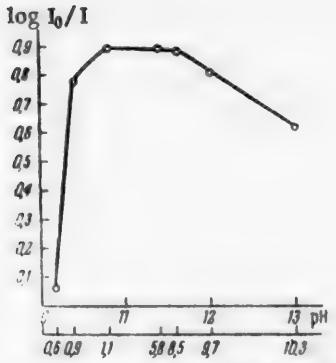

Fig. 2. The relation between the optical density of n-butanol extracts of thymolindophenol and the pH of the solution, before and after addition of thymol and hypobromite.

The absorption curves of solutions of the dye in n-butanol and in isoamyl acetate* are shown in Fig. 1. The arbitrary molar extinction coefficient of the dye in n-butanol is six times that in isoamyl acetate. Accordingly, by using n-butanol for extracting the dye, it is possible to increase the selectivity of the determination. A red filter ($\lambda_{effective}$ = mμ) should be used for measuring the optical density of the extracts.

2. Establishment of the acidity conditions. The optimum pH value for formation of the dye was established as follows. Equal amounts of ammonium sulfate solution were introduced into a series of flasks and alkali or acid added dropwise for establishing varying pH values, which were measured with an LP-3 pH-meter. An exactly similar series of solutions was then prepared, and thymol and hypobromite added to them. After 30 min the pH of each of them was measured. The dye formed was extracted with 20 ml of n-butanol, and the optical density of the extract measured in a cuvette with a layer thickness of 1 cm.

The results obtained are shown in Fig. 2.

Formation of the colored compound proceeds at pH 11-11.5. For the reaction to proceed successfully, the pH of the test solution should be adjusted to 1.5-8.5 prior to addition of the solutions of the reagents. In practice, good results are obtained on neutralizing the test solution to a phenolphthalein end point.

3. The use of masking agents. The hydroxides of a number of metals adsorb the dye formed and complicate its extraction with organic solvents. In addition, precipitation of such hydroxides as ferric hydroxide interferes with the neutralization of the solutions by alkali to the phenolphthalein end point. Accordingly, during the determination of small amounts of nitrogen it is necessary to prevent precipitation of the hydroxides by addition of appropriate materials.

Of the masking agents tested for iron (Seignette salt, oxalic acid, sodium ethylenediaminetetraacetate, phosphoric acid, and potassium fluoride), potassium fluoride proved to be the most suitable; it does not interfere with the thymol-hypobromite reaction for ammonia.

Potassium fluoride and hydrogen peroxide were tested as agents for prevention of titanium hydroxide precipitation. It was established that hydrogen peroxide in the amounts necessary for completely complexing titanium (0.15 M and upwards) interferes with formation of the dye. Good results were obtained on using potassium fluoride. When the latter is used, during extraction, as a result of a decrease in solubility following upon addition of n-butanol, a white crystalline precipitate of K_2TiF_6 separates out, but this does not interfere with the extraction.

For the determination of nitrogen in samples based on iron and titanium, it is necessary to add 2 ml of a 20% solution of potassium fluoride for completely complexing 0.01 g of iron, while for complexing 0.01 g Ti, 0.5 ml of the potassium fluoride solution should be added.

*The optical density of the solutions was measured on an FM-Pulfrich type photometer.

During determination of nitrogen in metallic chromium and its compounds, good results are obtained on using oxalic acid. Three g of oxalic acid is necessary for completely complexing 0.01 g Cr.

During storage, oxalic acid absorbs ammonia from the air; accordingly, only oxalic acid freshly recrystallized from twice distilled water should be used. When a high blank is obtained, recrystallization of the oxalic acid should be repeated.

Potassium fluoride can be used in addition to oxalic acid.

4. The effect of various metal ions on the thymol-hypobromite reaction. For the successful determination of small amounts of nitrogen in refractory compounds of titanium, chromium, iron, and vanadium, a study was made of the influence of these elements on the thymol-hypobromite reaction. For this purpose a series of calibration curves was constructed. The composition of the solutions used for constructing the calibration curves corresponded as closely as possible to that of the solutions obtained after dissolving aliquots of the test samples. Each of the solutions contained 2.5 ml of concentrated sulfuric acid and 2 g of potassium sulfate per 100 ml of solution. The solution used for constructing a calibration curve for nitrogen in the presence of titanium contained 0.08 g of titanium in the form of K_2TiF_6, while that used for determination of nitrogen in the presence of chromium contained 0.1 g chromium in the form of $CrCl_3$, that used for nitrogen in the presence of iron contained 0.1 g iron taken in the form of metallic iron, and that used for nitrogen in the presence of vanadium contained 0.1 g of vanadium in the form of V_2O_5.

Ten ml lots of one of these solutions were poured into a series of flasks, to which were then added various amounts (0.1, 0.2. . . 0.8 ml) of a standard ammonium sulfate solution containing 100 μg of nitrogen per ml. In addition, a separate calibration curve was constructed for solutions containing only sulfuric acid, potassium sulfate, and the standard ammonium sulfate solution.

To the solutions obtained was added a 20% potassium fluoride solution and the procedure described for the determination of nitrogen in titanium carbide then followed (see below).

Experiments showed that calibration curves constructed in the presence of titanium, iron, chromium, and vanadium hardly differ at all from the curves obtained under the same conditions with the pure ammonium salt. Accordingly, it is possible to determine small amounts of nitrogen in samples containing titanium, iron, chromium, and vanadium by constructing one general calibration curve, using a pure ammonium salt for its construction.

Below is given a technique for the determination of nitrogen in titanium carbide and boride which has been developed on the basis of the results obtained. Determination of nitrogen in refractory compounds based on chromium, iron, and vanadium only differs in the method used for decomposing aliquots of test sample and in the masking agent used for prevention of hydroxide precipitation.

In refractory chromium compounds nitrogen may be present as the nitrides Cr_2N and CrN. The nitride Cr_2N is readily decomposed on boiling an aliquot of sample with sulfuric acid 1 : 4, while the nitride CrN does not dissolve even on prolonged boiling of an aliquot with a mixture of concentrated sulfuric acid and potassium sulfate [8]. Fusion in this case would lead to volatilization of nitrogen. Since the test samples contain a very small amount of nitrogen compared with their chromium content, it is most likely that the nitrogen in a sample is in the form of Cr_2N. Accordingly, during the determination of nitrogen in refractory chromium compounds, the time for which an aliquot is boiled with sulfuric acid 1 : 4 is limited to two hours. Oxalic acid is added to keep chromium in solution.

During determination of nitrogen in metallic iron and its compounds, the sample is dissolved in sulfuric acid 1 : 4, with subsequent complexing of iron to a fluoride complex.

Since vanadium nitride is decomposed with a mixture of concentrated and potassium sulfate, an aliquot of test samples based on vanadium is boiled with the given mixture for six hours, the solution obtained being analyzed even if complete decomposition is not achieved. Potassium fluoride is used for keeping vanadium in solution.

Determination of nitrogen in titanium carbide. During determination of small amounts of nitrogen in titanium carbide, it is essential, as far as possible, to use chemically pure grade reagents, while all solutions should be prepared in twice distilled water (after adding $KMnO_4$ to a definite rose color and 5 ml of sulfuric acid 1 : 4; the middle fraction of the second distillation is taken).

When chemically pure sodium hydroxide is not available, a 40% solution of it which is free from nitrogen can be prepared as follows: to a 20% solution of sodium hydroxide is added 3-5 lumps of chemically pure zinc, and the solution evaporated by boiling until its volume has decreased to half its original value.

Thymol (2% solution) is prepared by dissolving 2 g of the chemically pure product, ground beforehand in a mortar, in 10 ml of 8% sodium hydroxide and adding 90 ml of water. The solution is kept in a dark vessel.

Sodium hypobromite is prepared by mixing 100 ml of saturated bromine water with 35 ml of 8% sodium hydroxide.

After use, n-butanol can be recovered by distillation, after adding anhydrous calcium chloride to it until saturation and removing the aqueous layer formed.

A standard solution containing 100 μg nitrogen per ml is prepared by dissolving in water 0.4717 g of $(NH_4)_2SO_4$ which has been recrystallized and dried over concentrated sulfuric acid. The solution is transferred to a 1 liter standard flask, and the volume made up to the mark with water.

Analytical procedure. A 0.1 g of titanium carbide is dissolved in 2.5 ml of concentrated sulfuric acid to which 2 g of potassium sulfate has been added; the aliquot is dissolved in a 50 ml flask which is covered with a funnel containing a plug of glass wool, in order to prevent sputtering. After dissolution is complete, the solution is transferred to a 100 ml standard flask, then diluted to the mark with water and thoroughly mixed. Ten ml of the solution obtained is transferred to a 50 ml flask, 0.5 ml of 20% potassium fluoride is added, followed by one drop of phenolphthalein solution; the solution is then neutralized with 8% sodium hydroxide solution until a stable rose color is obtained. Five ml of thymol solution is added and the solution mixed; 5 ml of hypobromite solution is added dropwise with constant stirring, and finally another 5 ml of thymol solution added. After 30 min, the solution is transferred to a 100 ml separating funnel and the blue dye formed extracted with n-butanol 2-3 times using 5-7 ml lots.

The extracts are filtered through a cotton wool plug into a 25 ml standard flask and the volume made up to the mark with n-butanol. The solution is shaken up and the color intensity of the solution obtained measured in a cuvette with a layer thickness of 1 cm.

The nitrogen content is found from a calibration curve constructed by means of the standard ammonium sulfate solution. A blank test is carried out at the same time as the analysis of test samples, taking all the reagents used through all the stages of the analysis.

During measurement of the optical density of the extracts obtained from aliquots of the samples, the extract obtained during the blank run is placed in the other cuvette as reference solution.

SUMMARY

A study has been made of the extraction with various organic solvents of the dye formed during the thymol-hypobromite reaction for nitrogen. n-Butanol gives the most intense color.

The optimum pH for formation of indothymol is 11. Prior to addition of thymol and hypobromite, the acid solutions of the test sample should be neutralized with sodium hydroxide to the phenolphthalein end point.

For prevention of hydroxide precipitation, oxalic acid is used in the case of chromium and potassium fluoride is used for iron, titanium, and vanadium. Iron, vanadium, and titanium as their fluoride complexes and chromium as its oxalate complex do not affect the thymol-hypobromite reaction. A method has been developed for the determination of small amounts of nitrogen (from 0.01 to 1%) in titanium carbide.

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ELEMENTAL ORGANIC ANALYSIS BY THE "WET COMBUSTION" METHOD*

COMMUNICATION II. RAPID DETERMINATION OF SILICON IN SILICOORGANIC COMPOUNDS

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Wet oxidation methods have been used for a long time for the analysis of silicoorganic materials [2]. Kreshkov and Nessonova [3] have pointed out that the conditions and the possibilities of oxidation by the wet method are specific for each organic material. Accordingly, in order to oxidize the esters of orthophosphoric acid they used potassium iodate in a sulfuric acid medium, while for diethyl- and diphenyldichlorosilane they used a more complicated mixture consisting of chromic anhydride and potassium iodate in a concentrated sulfuric and phosphoric acid medium. The silica formed in all cases was determined gravimetrically or colorimetrically in the form of blue silicomolybdate.

At present, determination of silicon in polysiloxanes is carried out by heating them with a mixture of 25% oleum and concentrated nitric acid containing 20% nitrogen oxides. The operation is carried out very carefully in order to avoid foaming and sputtering of test samples. After removing the nitrogen oxides and sulfuric acid, the quartz vessel in which oxidation is carried out is calcined to constant weight at 800° and the silicon content assessed from the weight of SiO_2. This method is characterized by the simplicity with which it can be carried out and by its high accuracy (0.2%); it takes a long time, however (7-8 hr) [4].

Šír and Komers [5] also decomposed silicoorganic materials with a mixture of oleum and fuming nitric acid, but a titrimetric finish was used for determining the silicon; this should speed up the analysis. Nevertheless, the necessity of fusing the silica formed with potassium and sodium carbonates in order to convert the SiO_2 to a soluble state increases the overall duration of an analysis.

Earlier [1] we developed a method for the determination of carbon and silicon in silicoorganic compounds on one aliquot. In contrast to the technique of Kreshkov and Nessonova [3], we carried out oxidation with concentrated sulfuric acid and a concentrated aqueous solution of chromium trioxide in an oxygen stream at 150°. Under these conditions even such stable materials as polysiloxanes were completely oxidized. Complete mineralization in the latter instance was achieved considerably more rapidly (30 min) than is possible by the existing method [4]. During the oxidation, resinification and sulfonation products were not formed, such compounds being often more stable to oxidation than the compounds originally taken. At the same time the mineralized silica was determined gravimetrically; this took 3-3.5 hr.

Thus, the short method of decomposing silicoorganic materials [1] ended in a long gravimetric determination of silica, while a rapid titrimetric finish was used in conjunction with prolonged decomposition [5].

Kalman and Vago [6] have successfully used a titrimetric determination of silicon in tetraethoxysilane. The method suggested by the authors is based on the hydrolysis of tetraethoxysilane in an alcoholic solution of hydrofluoric

*For Communication I, see [1].

TABLE 1

Determination of Silicon in Silicoorganic Compounds after Oxidation with a Chromic and Sulfuric Acid Mixture

Test compound	Sample wt., mg	0.1 N HCl used, ml	Si, %		Difference
			found	calc.	
1,8-Triethylethyloctasiloxane $C_{36}H_{90}O_7Si_8$	27,20 25,40	10,20 9,41	26,31 25,99	26,13	+0,18 −0,14
1,3,5,7-Diethylcyclotetrasiloxane $C_{16}H_{40}O_4Si_4$	28,45 26,70	11,20 10,41	27,62 27,35	27,48	+0,14 −0,13
Dimethyldidecyloxysilane $C_{22}H_{48}O_2Si$	90,60 90,40	9,61 10,00	7,44 7,76	7,54	−0,10 +0,22
Trimethyldecyloxysilane $C_{13}H_{30}OSi$	101,20 98,80	16,96 16,81	11,76 11,94	12,19	−0,43 −0,25
Phenyldibutoxychlorosilane $C_{14}H_{23}O_2SiCl$	46,50 48,00	6,46 6,81	9,75 9,95	9,79	−0,04 +0,16
Phenylmethylbutoxychlorosilane $C_{11}H_{17}OSiCl$	43,10 36,90	7,64 6,26	12,44 11,90	12,28	+0,16 −0,38

TABLE 2

Determination of Silicon in Technical Ethylpolysiloxanes

Sample designation	Sample wt., mg	0.1 N HCL used, ml	Si determined, %		Deviation between the methods, %
			by the method proposed	by the current method	
Type 5, batch 3	13,25 22,70	5,13 8,89	27,2 27,5	26,9	0,4
Type 4, batch 2	18,60 32,00	7,64 13,37	28,8 29,3	28,4	0,6
Liquid 1, batch 7	21,10 21,80	6,49 6,75	21,6 21,7	22,2	0,6
Liquid 2, batch 13	19,70 20,80	7,22 7,53	25,7 25,4	25,6	0,1
Liquid 3, batch 1	20,60 15,90	7,85 5,97	26,7 26,3	27,1	0,6
Liquid 5, batch 44	24,10 14,40	9,31 5,65	27,1 27,5	26,9	0,4

*The analyses were carried out by L. M. Kharchevnikova.

acid, with subsequent titration of the potassium fluorosilicate formed. A determination takes 20-30 min. This method, however, is only suitable for the analysis of monomeric and polymeric ethoxysilanes.

In the work described here, in order to speed up the determination of silicon in silicoorganic compounds, use was made of a method used by us earlier in which various organic and heteroorganic compounds were mineralized with a mixture of chromic and sulfuric acids [1]. The silica formed under these conditions was filtered off[3],

TABLE 3

Determination of Silicon in Readily Hydrolyzable Silicon-Containing Compounds

Test material	Sample wt., mg	0.1 N HCl used, ml	Si, %		Difference
			found	calc.	
Triethoxysilane	49.55	12.23	17.30	17.10	+ 0.20
$C_6H_{16}O_3Si$	49.70	11.98	16.90		− 0.20
Silicon tetrachloride	41.85	9.93	16.64	16.53	+ 0.11
$SiCl_4$	50.08	12.03	16.85		+ 0.32

dissolved in a concentrated alkali solution, and the silicon subsequently determined titrimetrically using Sir and Komers' method [5]. In the case of the analysis of ethoxysilanes or chlorosilanes (not containing radicals), which are readily hydrolyzed by aqueous solutions of alkali with formation of sodium silicate, silicon determination is further simplified, since there is no need to heat with the acid mixture.

Analytical procedure. An aliquot of the silicoorganic material is placed in a 100 ml short-necked, pear-shaped flask containing 10 ml of concentrated sulfuric acid and 2-3 ml of chromic acid (70 g CrO_3 is dissolved in 100 ml of water) added dropwise with continuous stirring; the mixture is heated for 30 min at 150-160°. The flask is cooled (external cooling with water is not used) and 30-40 ml of water added. The solution obtained is boiled for 5 min at 110-120°. If the solution is not observed to boil at 120°, the flask should be cooled and some water added, after which the solution is heated up again. If, on the other hand, boiling is observed to start below 110°, the solution is evaporated until a temperature of 110-120° is reached. When heating is complete, the solution is cooled to 70-60°, 1-1.5 ml of a 2% gelatin solution added with vigorous stirring, and the solution allowed to stand for 5-10 min for complete coagulation of the silica. The precipitate is filtered off through an ashless, loose filter paper (7 cm) and washed with hot distilled water.

The filter paper plus precipitate are transferred to a polyethylene beaker,* 5-7 ml of a 30% NaOH solution is added until the precipitate has dissolved completely, 5-6 drops of indicator is added,** and the solution neutralized, first of all with hydrochloric acid 1 : 1, and then with hydrochloric acid 1 :10 to a weak acid reaction; the solution obtained is transferred to a conical flask and accurately neutralized with 0.1 N solutions of acid and alkali. At this stage the total volume should not exceed 40-50 ml. The solution is then saturated with neutral potassium chloride in order to prevent hydrolysis of the fluorosilicate, 10 ml of a neutral solution of ammonium fluoride is added,*** followed by 20 ml of 0.1 N hydrochloric acid, and excess of the latter finally titrated with 0.1 N alkali solution.

The method has been checked on a series of individual silicoorganic compounds (Table 1).

Silicon was determined in technical ethylpolysiloxanes by the suggested method. The results of the analyses agree well with the data obtained by the existing method [4] (Table 2).

*Filtration can be conveniently carried out through a polyethylene funnel and the precipitate dissolved on it in alkali; the solution is collected in this case in a beaker made from nonsilicon material.

**The indicator is made by mixing two solutions; a) a 0.1% alcoholic solution of methyl red; b) to 100 ml of a 0.1% solution of bromocresol green in 20% alcohol is added 0.57 ml of 0.1 N HCl or NaOH. Five parts of solution "a" are mixed with seven parts of solution "b."

***The 1% ammonium fluoride solution is prepared by mixing 20 ml of 25% ammonia solution and 12.5 ml of 40% HF, with cooling, in a polyethylene flask. The mixture obtained is diluted with water to 500 ml and, after rough neutralization, the solution is finally accurately neutralized with standard 0.1 N alkali and acid solutions. The neutrality of the solution thus prepared is checked daily as follows. Twenty ml of 0.1 N hydrochloric acid and 10 ml of the ammonium fluoride solution are titrated with 0.1 N alkali in the presence of 4-5 drops of indicator. When the amount of alkali used differs from the amount of alkali used for titrating 20 ml of acid, the ammonium fluoride solution is neutralized again.

Table 3 contains examples of determination of silicon without preliminary oxidation. In these cases, an aliquot of test material was hydrolyzed in 15% NaOH solution in a polyethylene flask. The solution was neutralized and titrated as described above. We should like to point out that in the case of compounds of this type it is also possible to determine hydrogen linked to silicon, as well as silicon, on one aliquot of sample [7].

SUMMARY

A rapid method for the determination of silicon in silicoorganic compounds has been developed; it is based on their oxidation with a mixture of chromic and sulfuric acids at 150°. The silica thereby formed is filtered off, dissolved in alkali, and converted into fluorosilicate ions in the presence of excess acid, excess of which is back titrated with alkali. A determination takes 1.5 hr. Determination of silicon in compounds which are readily hydrolyzed by aqueous alkali solutions to form silica takes 30 min.

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MICROANALYSIS OF MERCUROORGANIC COMPOUNDS

COMMUNICATION I. DETERMINATION OF CARBON, HYDROGEN, AND MERCURY IN ORGANIC COMPOUNDS NOT CONTAINING HALOGENS

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Little attention is given to the elemental microanalysis of mercuroorganic compounds in modern textbooks. The methods in current use for the analysis of such compounds are characterized by their complexity: in most cases a special filling has to be used in the combustion tube; the whole procedure is tiresome and takes a long time. The mercury absorbent used in almost all the current techniques is gold, which, after three to five analyses, has to be regenerated [1-7]. All that has been said above compelled us to develop a more convenient and rapid method for the analysis of mercuroorganic compounds.

First of all we investigated the possibility of determining carbon, hydrogen, and mercury in mercuroorganic compounds on one aliquot. Combustion was carried out in the usual quartz tube; the undecomposed pyrolysis gases were passed over platinum contacts heated to 900°. The mercury vapors were absorbed in a small quartz tube filled with gold turnings, this tube being connected to the combustion tube via a ground joint. The quartz tube was followed by absorbents – anhydrone and askarite. These experiments gave unsatisfactory results.

In the work described here we decided to examine the possibility of carrying out an elemental microanalysis of mercuroorganic compounds without using gold.

We examined the thermal decomposition product of $AgMnO_4$, prepared by Korbl's method [8], as an absorber for mercury. The Korbl catalyst was placed in a quartz apparatus, heated to 105-110°, and connected to the combustion tube via a ground joint. Absorbers filled with anhydrone and askarite followed. Platinum contacts were placed in the combustion tube, which was heated to 900°. We were unable, however, to obtain acceptable results during the analysis of mercuroorganic compounds in such a system. Apparently, the main reason for this lack of success was the use of a ground joint which was not lubricated and was heated in order to expel the mercury vapors. Finally, having abandoned the idea of determining carbon, hydrogen, and mercury simultaneously on one aliquot, we decided to determine carbon and hydrogen on one aliquot and mercury on another.

The carbon and hydrogen were determined in a quartz combustion tube. In the first series of experiments, the platinum contacts were placed in the tube in the zone heated by a large electric oven to 900°. Close to the tip was placed a layer of the thermal decomposition product of $AgMnO_4$, heated to 105-110° with an auxiliary electric oven. The $AgMnO_4$ decomposition product was followed by a layer of silver on pumice. The pumice served to hold back the very small particles of dust carried through from the Korbl catalyst by the oxygen stream. In the very tip of the tube was fitted a lump of silver wire. The results obtained during combustion in a tube filled in this way are given in Table 1.

As is evident from the results given in Table 1, when a tube packed in this way is used, acceptable results are obtained.

TABLE 1

Test material	Sample wt., mg	Found, %		Calc., %		Error, %	
		C	H	C	H	C	H
Diphenyl mercury $(C_6H_5)_2Hg$	6,950	40,64	3,12	40,61	2,84	+0,03	+0,28
	5,080	40,50	3,08			−0,11	+0,24
Dinaphthyl mercury $(C_{10}H_7)_2Hg$	7,240	52,73	3,24	52,79	3,10	−0,06	+0,14
	4,930	52,58	3,09			−0,21	−0,01
Phenyl-p-vinylphenyl mercury $p\text{-}CH_2{=}CH\text{-}C_6H_4Hg\,C_6H_5$	7,540	43,83	3,47	44,15	3,16	−0,32	+0,31
	5,490	43,99	3,46			−0,16	+0,30
Phenyl mercury methacrylate $C_6H_5HgOCOC(CH_3){=}CH_2$	4,720	33,07	3,13	33,10	2,78	−0,03	+0,35
	8,330	32,99	2,96			−0,11	+0,18
Phenyl mercury acrylate $C_6H_5HgOCOCH{=}CH_2$	5,190	30,97	2,63	30,99	2,31	−0,02	+0,32
	6,250	30,70	2,42			−0,29	+0,11

TABLE 2

Test material	Sample wt., mg	Found, %		Calc., %		Error, %	
		C	H	C	H	C	H
Dinaphthyl mercury $(C_{10}H_7)_2Hg$	5,520	52,65	3,16	52,79	3,08	−0,14	+0,08
	4,050	52,96	3,12			+0,17	+0,04
Diphenylmercury $(C_6H_5)_2Hg$	5,370	40,65	3,12	40,62	2,84	+0,03	+0,03
	5,120	40,46	3,12			−0,16	−0,16
Phenyl mercury methacrylate $C_6H_5HgOCOC(CH_3){=}CH_2$	12,020	33,15	2,86	33,10	2,78	+0,05	+0,12
	7,270	33,22	3,05			+0,08	+0,27
Phenyl mercury acrylate $C_6H_5HgOCOCH{=}CH_2$	4,940	31,16	2,73	30,99	2,31	+0,17	+0,12
	5,490	30,92	2,59			−0,07	+0,28

In succeeding experiments it was established that combustion of mercuroorganic compounds is readily carried out without using platinum contacts, while the temperature of the electric oven used for heating the thermal decomposition product of $AgMnO_4$ can be lowered to 60°; the other conditions were left unchanged. Absorption of mercury and its oxides was carried out on the same layer (14 cm) of the thermal decomposition product of $AgMnO_4$ as in the previous series of experiments.

Results of experiments on the combustion of mercuroorganic compounds in which platinum contacts were not used, and in which the temperature of the auxiliary oven used for heating the layer of thermal decomposition product of $AgMnO_4$ was 60°, are given in Table 2.

From the results given it is evident that the values obtained for hydrogen are somewhat high, but the error, on an average, is smaller than when the layer of $AgMnO_4$ decomposition product is heated at a higher temperature. When the layer is not heated enough very low results were obtained for hydrogen.

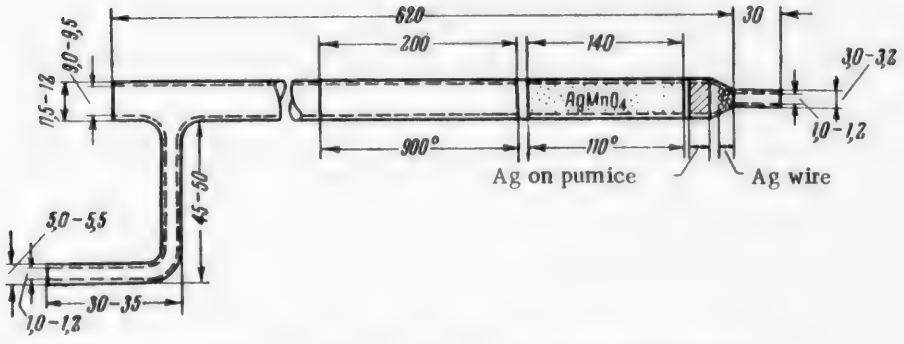
The constant positive error in the hydrogen determination is, presumably, explained by negligible traces of mercury getting into the anhydrone absorber [9].

Korbl's catalyst has the advantage that it is readily available and can be used without regeneration and without replacement for a long time. After 100-120 determinations (for samples containing about 50% mercury) one starts to get low results for hydrogen; this indicates that it is time to replace the catalyst.

The mercury was determined on a separate aliquot of the mercuroorganic compound by burning it in a flask filled with oxygen and then dissolving mercury and its oxides in concentrated nitric acid [10]. The mercury was finally determined titrimetrically. The solution, after appropriate treatment, was titrated with ammonium thiocyanate using ferric alum as indicator [11].

TABLE 3

Test material	Sample wt., mg	Hg found, %	Hg calc., %	Error, %
$(C_6H_5)_2Hg$	5,510	56,17		—0,37
	5,790	56,53	56,54	—0,01
$(C_{10}H_7)_2Hg$	6,010	44,46		+0,36
	3,660	44,11	44,10	—0,01
$P\text{-}C_{11}H_{12}Hg$	3,405	52,32		—0,30
	3,190	52,35	52,68	—0,36
$C_{10}H_{10}HgO_2$	4,390	55,03		—0,26
	6,210	54,86	55,29	—0,43
$C_8H_8HgO_2$	3,950	57,50		—0,02
	4,170	57,60	57,52	+0,08



Tube packed for analysis of organic compounds containing mercury.

The normality of the ammonium thiocyanate was checked against 0.01 N mercuric nitrate which was added to the working solution, i.e., to distilled water containing potassium permanganate, hydrogen peroxide, and an amount of HNO_3 equal to that used for dissolving the mercury and its oxides in each experiment (see experimental section). This technique is a necessary condition for obtaining accurate results [12]. Results of mercury determinations are given in Table 3.

From these results it is clear that the method of determining mercury by combustion in flasks filled with oxygen (Schöniger), followed by titration of mercuric nitrate with ammonium thiocyanate, is reasonably accurate (error ± 0.5%), requires simple apparatus, and is rapid. When combustion by the Schöniger technique is carried out in parallel with determination of carbon and hydrogen, determination of carbon, hydrogen, and mercury takes about 1.5 hr, while, for example, it takes about one hour simply to mineralize an aliquot of a mercuroorganic compound with sulfuric acid [13].

Determination of carbon and hydrogen. The quartz combustion tube (see diagram), after the usual preparation and drying, was packed as follows: into the tip of the tube was placed a lump of silver wire (d = 0.04 mm); next to this was placed a layer of $AgMnO_4$ (about 10 g) heated beforehand in an oxygen stream for two hours at 540°. The layers were separated by packings of calcined asbestos. By means of an auxiliary electric oven the temperature of the $AgMnO_4$ layer was kept within the range 105-110° in the first series of experiments, and within the range 60-65° in the second series. In the first series of experiments, platinum contacts (5 cm) were placed in the zone of the combustion tube heated to 900° by a large electric oven; in the second series of experiments this part of the tube was left empty. A blank run took 25 min. An aliquot of sample (5-8 mg) was placed in a small quartz tube 6.5 cm long and 0.5 cm in diameter. Combustion was carried out in an oxygen stream with a throughput of 18-20 ml/min, and lasted about 15 min. Purging was carried out for 10 min, after which the absorbers (anhydrone and askarite) were removed and weighed 10 and 15 min afterwards, respectively.

Determination of mercury. Reagents. 1. Mercuric nitrate (0.01 N solution). An accurately weighed amount of purified [14] mercury metal (about 1.0030 g) was dissolved by heating in 50 ml of concentrated nitric acid; after cooling, the solution was made up to the mark with distilled water.

2. Ammonium thiocyanate (0.01 N solution). The normality of the ammonium thiocyanate solution was determined as follows: 5 ml of 0.01 N $Hg(NO_3)_2$ solution was pipetted into a flask and 25 ml of twice distilled water, 3 ml of concentrated HNO_3, one drop of a 5% $KMnO_4$ solution, one drop of dilute (about 5%) H_2O_2, and 1 ml of a saturated solution of ferric alum added. The mixture was titrated with 0.01 N NH_4SCN to the appearance of a rose-yellow color.

Experimental procedure. An aliquot of the mercuroorganic compound (3-6 mg) was wrapped up in filter (ashless) paper; the latter was attached to a platinum wire fused into the stopper of the combustion flask and ignited in a 300 ml Erlenmeyer flask filled with oxygen [10, 15-17]. Three ml of concentrated nitric acid had been placed in the flask beforehand. After combustion of the aliquot the flask was allowed to stand for 30 min. The flask was then carefully opened, the stopper and the flask walls were rinsed with twice distilled water, and a 5% $KMnO_4$ solution was added dropwise, with stirring, until a rose color which was stable for five min was obtained. Excess permanganate was destroyed by careful dropwise addition of 5% H_2O_2, and, after addition of 1-1.5 ml of a saturated ferric alum solution, the solution was titrated with 0.01 N NH_4SCN from a microburet to the appearance of a rose-yellow color.

One ml of 0.01 N NH_4SCN solution corresponds to 1.003 mg Hg.

The method is applicable for the determination of mercury in mercuroorganic compounds which do not contain chlorides and bromides.

SUMMARY

A micromethod has been developed for the determination of carbon and hydrogen in mercuroorganic compounds by burning them in a stream of oxygen in a quartz tube containing the thermal decomposition product of $AgMnO_3$ heated to 60°. The experimental error does not exceed the permissible norms.

A rapid micromethod has been developed for the determination of mercury in mercuroorganic compounds not containing halogens; it is based on a Schöniger combustion, the reaction products being absorbed by concentrated HNO_3; the Hg^{2+} formed is finally titrated with 0.01 N NH_4SCN using ferric alum as indicator. The experimental error is ± 0.5%.

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THE USE OF ACETIC ANHYDRIDE AS A DIFFERENTIATING SOLVENT FOR THE SEPARATE ACIDIMETRIC TITRATION OF AMINES, SULFOXIDES, AND AMIDES

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Nonaqueous solvents which bring out the acid or basic properties of organic compounds which normally appear neutral in aqueous solutions have found wide application in organic functional analysis in the last ten years. The number of nonaqueous solvents used as media for titration is very large and their choice is determined by the character of the materials to be analyzed and the aims pursued by the research worker [1, 2]. A detailed consideration of the theoretical bases and the history of the application of nonaqueous solvents in quantitative analysis are given in N. A. Izmailov's book [3].

Nonaqueous solvents used for acid–base titration can be divided into two types; ones which level, and those that differentiate the strengths of acids and bases. The first type permits determination of the sum of the components in one sample, while the second type permits determination of each component of the test mixture. At present, for materials which are basic in character, the following are used as differentiating solvents: acetonitrile, dioxane, glycols, and ketones. By using a solution of perchloric acid in these solvents it is possible to titrate individually mixtures of alkaloids [4], aliphatic and aromatic, and aliphatic and heterocyclic amines [5]. In the solvents listed, however, it is only possible to titrate those bases whose dissociation constant (in H_2O) is not less than 10^{-11}-10^{-12}.

In the present article a description is given of the use of acetic anhydride as a differentiating solvent for materials which are basic in character.

Acetic anhydride, the arbitrary pH value of which, according to Usanovich [6], lies within the limits of 1 and 3, permits the titration, as bases, of compounds with a dissociation constant (in H_2O) of the order of 10^{-14} - 10^{-15}, i.e., compounds which are neutral in aqueous solutions.

Until recently, acetic anhydride has only had limited application as a nonaqueous solvent, mainly as a dehydrating reagent for the titrants and as one of the components during titration in mixed solvents. It has been shown in a number of papers by Soviet and foreign authors that addition of acetic anhydride in amounts of 5-20% with respect to acetic acid, nitromethane, and acetonitrile significantly increases the definition of the titration of weak organic bases [7-9].

The first to use acetic anhydride as a solvent for nonaqueous titration was Gremillion [10], who showed that such materials as diphenylamine [$K_0(H_2O) = 6.3 \cdot 10^{-14}$], urea [$K_0(H_2O) = 1.5 \cdot 10^{-14}$], and thiourea [$K_0(H_2O) = 1.1 \cdot 10^{-15}$], behave as bases in acetic anhydride. In 1958 Wimer published two papers on the titration of carboxylic and phosphoric acid amides [11] and of sulfoxides [12] in an acetic anhydride medium.

We came up against the differentiating action of acetic anhydride during a study of nitrogen bases isolated from petroleum. During this study it was first found that during the potentiometric acidimetric titration of mixtures

Results of Titration of Mixtures of Amines, Sulfoxides, and Amides in Acetic Anhydride by a Solution of 0.1 N $HClO_4$ in Dioxane

Composition	Sample wt., mg	Calculated, mg				Found, mg			
		N-aliphatic amines	N-aromatic and heterocyclic amines	S-sulfoxides	N-amides	N-aliphatic amines	N-aromatic and heterocyclic amines	S-sulfoxides	N-amides
Dimethyldecylamine •	29,60	2,00		—	—	1,97	—	—	—
Diethylaniline	36,30		3,52	—	—		3,56	—	—
Dimethyldecylamine	39,60	2,68		—	—	2,68		—	—
α-Hydroxyquinoline	29,00	—	2,80	—	—		2,81	—	—
α-Hydroxyquinoline	39,60	—	3,82	—	—	—	3,82		—
Dibenzylsulfoxide	61,20	—		7,50	—	—		7,50	—
α-Hydroxyquinoline	20,50	—	1,98		—	—	2,01		—
Dibenzylsulfoxide	10,30	—		1,43	—	—		1,41	—
Quinoline	40,00	—	4,33	—		—	4,31	—	
α-Acetonaphthalide	37,00	—		—	2,79	—		—	2,79
1-Ethyl-1,2,3,4-tetrahydroquinoline	33,30	—	2,90	—		—	2,88	—	
β-Acetonaphthalide	30,00	—	—	—	2,26	—	—	—	2,28
Dibenzylsulfoxide	61,80	—	—	8,59		—	—	8,58	
β-Acetonaphthalide	36,60	—	—		2,76	—	—		2,78
Dibenzylsulfoxide	30,50	—	—	4,24		—	—	4,18	
p-Bromoacetanilide	35,20	—	—		2,30	—	—		2,28
Allylbenzylsulfoxide	30,50	—	—	5,23		—	—	5,16	
β-Acetonaphthalide	31,00	—	—		2,34	—	—		2,31
Dibenzylsulfoxide	53,80	—	—	7,48		—	—	7,48	
α-Acetonaphthalide	36,00	—	—		2,71	—	—		2,71
α-Hydroxyquinoline	33,20	—	3,21			—	3,20		
Dibenzylsulfoxide	33,80	—		4,70				4,66	
α-Acetonaphthalide	57,00	—			4,30	—			4,29
1-Ethyl-1,2,3,4-tetrahydroquinoline	31,70	—	2 76				2,71		
Dibenzylsulfoxide	30,70	—		4,27				4,17	
β-Acetonaphthalide	31,80	—			2,40				2,39
Triethylamine	33,00	4,57				4,56			
α-Hydroxyquinoline	43,40		4,19				4,14		
Dibenzylsulfoxide	111,90			15,56				15,50	
β-Acetonaphthalide	30,50				2,29				2,29
Dimethyldecylamine	30,10	2,04				2,02			
1-Ethyl-1,2,3,4-tetrahydroquinoline	69,07		6,07				6,13		
Allylbenzylsulfoxide	63,60			10,92				10,76	
p-Bromoacetanilide	47,70				3,11				3,11

• All the test materials used for analysis were chemically pure. The dimethyldecylamine contained 6.78% instead of 7.56% N, and was not purified.

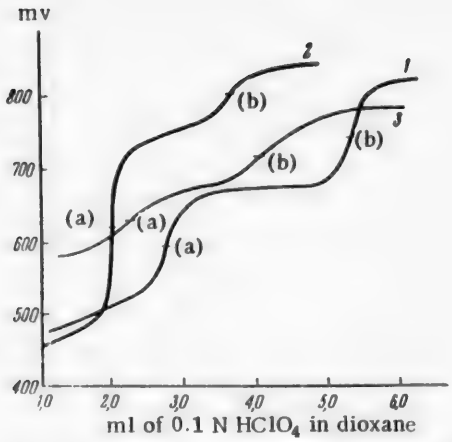

Fig. 1. Titration of two-component mixtures. 1) α-Hydroxyquinoline (a); dibenzylsulfoxide (b), 2) 1-ethyl-1,2,3,4-tetrahydroquinoline (a), β-acetonaphthalide (b); 3) dibenzylsulfoxide (a), α-acetonaphthalide (b).

containing heterocyclic bases (pyridines, quinolines, and thiazoles) and sulfoxides, there were two potential jumps, the first of which corresponded to completion of titration of the base, and the second the completion of titration of the sulfoxides.

The possibility of using acetic anhydride as a differentiating solvent for organic bases was then studied in more detail.

It was shown that it is possible, using acetic anhydride as the medium, to titrate each component of a mixture containing four types of compounds in one aliquot, the mixture consisting of: aliphatic amines, aromatic amines (or heterocyclic bases), sulfoxides, and carboxylic acid amides. The potentiometric titration curves of mixtures containing all four types of compounds exhibit four potential jumps; the first corresponded to completion of titration of the aliphatic amines, the second to aromatic (or heterocyclic) amines, the third to sulfoxides, the fourth to amides. During titration of two- and three-component mixtures, the titration curve has, respec-

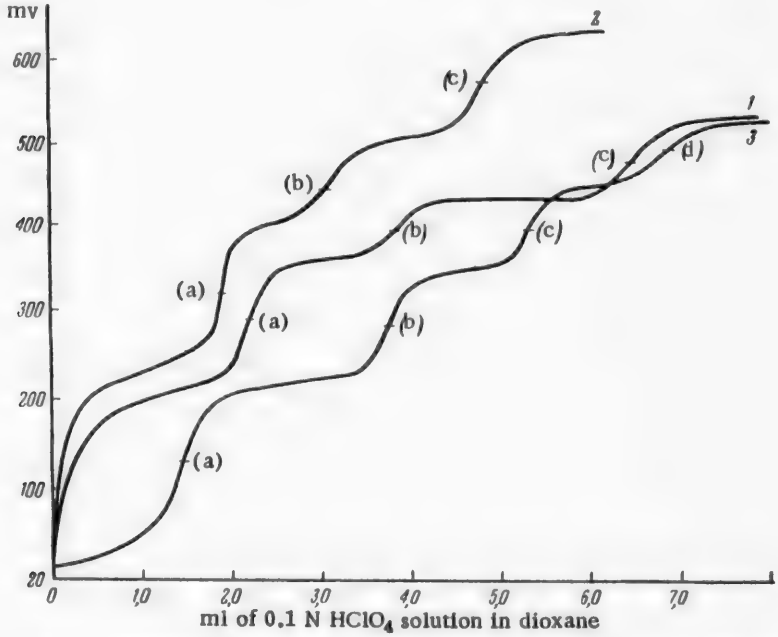

Fig. 2. Titration of three- and four-component mixtures. 1) α-hydroxyquinoline (a), dibenzylsulfoxide (b), α-acetonaphthalide (c); 2) 1-ethyl-1,2,3,4-tetrahydroquinoline (a), dibenzylsulfoxide (b), β-acetonaphthalide (c); 3) dimethyldecylamine (a), 1-ethyl-1,2,3,4-tetrahydroquinoline (b), allylbenzylsulfoxide (c), p-bromoacetaniline (d).

tively two and three potential jumps. In order to check the accuracy and reproducibility of the titrations, we made some mixtures containing aliphatic amines–aromatic amines, aliphatic amines heterocyclic base, heterocyclic base–sulfoxide, sulfoxide–amide, and also mixtures containing three and four components.

The results obtained are given in the table. The titration curves of some of the mixtures are given in Figs. 1 and 2.

In making up the synthetic mixtures, the choice of amines was naturally limited to those which are not acetylated by acetic anhydride (as Gremillion points out [10], acetylation can be avoided by titrating at 0°).

The titrant used was a solution of perchloric acid in dioxane. The use of a solution of perchloric acid in acetic acid, which behaves as a leveling solvent for the bases tested, lowers the differentiating effect of acetic anhydride; in this case, as a rule, the sum of the bases is titrated and the titration curve exhibits only one potential jump.

EXPERIMENTAL METHOD

Reagents: acetic anhydride, analytical or chemically pure grade; dioxane was treated beforehand with solid NaOH or KOH and distilled over Na metal [13]; 0.1 N or 0.05 N $HClO_4$ in dioxane (0.1 N $HClO_4$ solution was prepared by dissolving 7.5 g of 70% $HClO_4$ in one liter of dioxane). The normality of the $HClO_4$ solution was checked against a standard solution of potassium hydrogen phthalate or methyloctadecylamine in acetic acid.

Titration was carried out using an LP-5 potentiometer. The electrodes used were glass and a saturated calomel electrode connected to the titration vessel through a bridge filled with a saturated solution of LiCl in glacial acetic acid. The solution was stirred during titration with a glass stirrer driven by an electric motor.

Analysis. An aliquot of test mixture containing from 0.0001 to 0.001 M of each component was dissolved in 50-75 ml of acetic anhydride and titrated with a 0.1 N or 0.05 N solution of $HClO_4$ in dioxane, the titrant being added in 0.1 ml portions. When the test material was sparingly soluble in acetic anhydride, it was dissolved in a small amount of nitromethane, dioxane, or chlorobenzene; acetic anhydride was then added and titration carried out. A small amount of these solvents does not affect the definition of the titration.

During titration, the solution either remained colorless or acquired a weak yellow color, and only after adding the last 0.1 ml did the color change to a brown-black shade. The sharp color change could be used for establishing the titration end point during the titration of a mixture of unknown composition.

SUMMARY

It has been shown that acetic anhydride is a differentiating solvent for organic bases. In acetic anhydride as the medium, and using one aliquot of sample, it is possible to successively titrate aliphatic amines, aromatic (or heterocyclic) amines, sulfoxides, and carboxylic acid amides.

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BRIEF COMMUNICATIONS

DETERMINATION OF SMALL AMOUNTS OF BUTADIENE BY A PHOTOMETRIC METHOD

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In order to study the dimerization kinetics of butadiene it is necessary to determine small amounts of butadiene in the presence of the butadiene dimer (vinyl-1-cyclohexene-3) and n-hexane or n-heptane. It has been shown [1-6] that diene hydrocarbons with a conjugated system of double bonds can be quantitatively determined by their interaction with aromatic diazo compounds in the presence of polymerization products, and also of paraffin hydrocarbons. Isakova [7-9] has suggested a photometric method for the determination of small amounts of butadiene. The method is based on the interaction of butadiene with diazotized p-nitroaniline hydrochloride with formation of a colored compound, and subsequent measurement of the optical density on a photocolorimeter. Nevertheless, there are no detailed published results on the determination of butadiene by a photometric method, nor information on the possibility of using this method for the determination of butadiene in the presence of its dimerization products and paraffin hydrocarbons. In order to check on this method, conditions were developed for preparing p-nitroaniline hydrochloride, preparing diazotized p-nitroaniline hydrochloride, and carrying out the reaction between butadiene and the diazotized p-nitroaniline hydrochloride.

According to the method suggested [7-9], in order to prepare a 0.2% solution of p-nitroaniline hydrochloride, 6 ml of concentrated hydrochloric acid was taken for 2 g p-nitroaniline. It was found that the amount of hydrochloric acid indicated was obviously insufficient, and the p-nitroaniline hydrochloride could not be dissolved in water even on heating at 60°. It was found necessary to double the amount of hydrochloric acid. The p-nitroaniline hydrochloride solution was prepared as follows. To 2 g of p-nitroaniline was added 12 ml of concentrated hydrochloric acid and the mixture allowed to stand for one hour. 86 ml of water was then added and the solution heated to 60°; it was then quantitatively transferred to a 1 liter flask. Nine hundred ml of water heated to 50° was then added to the flask. After cooling to room temperature, the solution was made up to the mark. On standing, crystals separated from solution; accordingly, before use, it was necessary to filter the necessary amount of solution through filter paper.

Diazotization of the p-nitroaniline hydrochloride was effected at 15-20°, 40 ml of 0.1% sodium nitrite solution being added rapidly with vigorous stirring to 40 ml of the 0.2% p-nitroaniline hydrochloride solution. No color formation should be observed on pouring the solutions together. The solution was prepared immediately prior to the azo coupling reaction with butadiene.

In order to determine butadiene photometrically, a calibration curve was constructed using pure butadiene. Several measurements were carried out on samples kept in sealed ampoules in the case of mixtures of butadiene with n-hexane or n-heptane.

Butadiene regenerated from tetrabromobutane by the action of granulated zinc in an alcoholic medium was used for the work [10]. Tetrabromobutane was prepared by brominating gas containing 90% butadiene and 10% n-butylenes. Butadiene was accurately measured out into the reactor, and also analysis of butadiene from ampoules

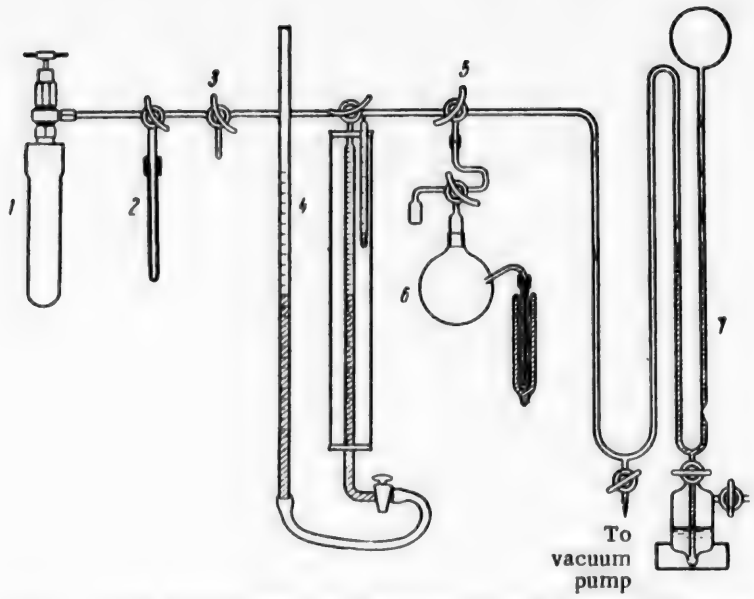

Fig. 1. Setup for measuring and determining small amounts of butadiene.

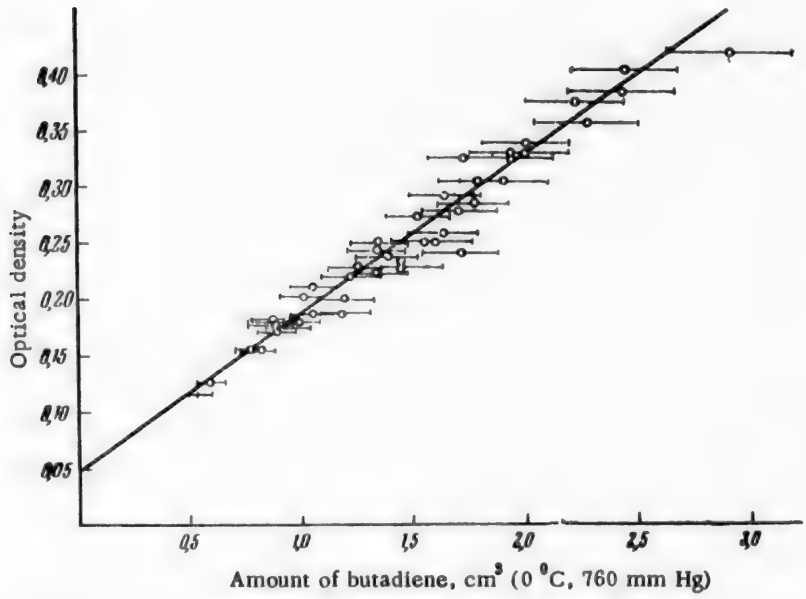

Fig. 2. Relation between optical density of the solution and amount of butadiene.

was carried out in the setup shown in Fig. 1. The setup consisted of a steel autoclave 1 for storing butadiene, a glass ampoule 2, a microburet 4 with a volume of 10 cm^3 and scale divisions of 0.02 cm^3, and a manometer 7.

Prior to a determination, the microburet was filled with mercury and the air evacuated from the setup by a vacuum pump. An aliquot of butadiene was transferred from the autoclave 1 into the ampoule 2, which was cooled with liquid nitrogen. Subsequently, the ampoule containing the butadiene was unfrozen and the gas passed into the microburet so that a pressure somewhat higher than atmospheric was established in the system. The excess gas pressure in the system was released through tap 3 and the volume of gas in the buret measured, as well as the temperature of the

Determination of Butadiene in the Presence of Butadiene Dimer (temperature 250°)

Duration of reaction, sec × 10^{-3}	Reaction velocity constant, $cm^3\ mole^{-1}\text{-}sec^{-1}$	Vol. of ampoule, cm^3	Amt. of butadiene, cm^3, 0°, 760 mm Hg		
			before reaction	after reaction	
				calc.	found experimentally
10.65	1.2	1.20	1.37	0.64	0.69
4.68	1.2	2.46	2.26	1.54	1.43
11.77	2.2*	2.48	1.90	0.93	1.00

*Temperature 260°.

surrounding air and the atmospheric pressure. A glass reactor 6 consisting of a 100 ml round bottom flask with a three way tap was connected to tap 5. When gas contained in an ampoule was to be measured, a flask with a glass outlet tube for connecting it to the opened ampoule was used. The air was evacuated from the reactor and the gas from the buret quantitatively transferred into it by cooling with liquid nitrogen. Accurate measurement of the gas in the reactor was controlled on the basis of the mercury level in the manometer. The gas in the reactor was defrosted and the diazotized p-nitroaniline hydrochloride solution sucked in through the three way tap, this solution having been prepared immediately prior to passing it into the reactor as described above. The reactor was disconnected from the setup and shaken for 10 min at 15-20°. The solution was quantitatively transferred to a 100 ml standard flask and its volume made up to the mark with water; after 10 min the optical density of the yellow solution was measured on an FÉK-M photocolorimeter with a blue filter, using 30 mm cuvettes; the reference solution was distilled water.

For determination of butadiene in its mixtures with n-hexane and n-heptane from sealed ampoules, the contents of the ampoule were frozen with liquid nitrogen; the top of the ampoule was opened and connected via a rubber tube with the side tube of the reactor 6, the ampoule was immersed in liquid nitrogen and the air pumped out of the ampoule and the reactor. The reactor was disconnected from the setup by means of the three way tap 5, and the contents of the ampoule transferred into it quantitatively by cooling the reactor with liquid nitrogen and warming the ampoule. The analytical procedure subsequently followed was the same as that used for the determination of pure butadiene, but with the difference that after making up the volume to the mark in the 100 ml standard flask, the layer of n-hexane or n-heptane was sucked off with a syringe, and the solution filtered through filter paper prior to introducing it into the cuvette.

On the basis of 43 values of the optical density of solutions obtained for amounts of butadiene from 0.53 to 2.9 cm^3 (0°, 760 mm) a calibration curve was constructed within the coordinates optical density – amount of butadiene in cm^3 by the method of least squares (Fig. 2). The mean probable error of a single measurement was ± 7%.

The possibility of using the photometric method for determining butadiene in the presence of the butadiene dimer was checked. For this purpose experiments were carried out on the dimerization of butadiene in the gaseous phase at 250 and 260°. An accurately measured amount of butadiene was sealed in an ampoule. The exact amount of butadiene was introduced into the ampoule by the same method as that used for introducing it into the reactor (Fig. 1, 6), the ampoule being connected to tap 5 instead of the reactor. After measuring out the butadiene into the ampoule, the latter was disconnected from the setup by means of tap 5 and sealed up.

Dimerization was carried out in a thermostat which was a carefully thermally insulated copper block. The heating of the thermostat was automatically controlled by means of a "Siemens" apparatus connected into the circuit of the heating spirals of the thermostat. The temperature was measured directly on the ampoule by means of a double junction chromel-copel thermocouple. The thermostat enabled the temperature to be kept constant up to 270° with an accuracy of ± 0.3°.

The ampoule was immersed in the thermostat which had been brought to the experimental temperature beforehand. The reaction time was counted from the moment when the ampoule was immersed in the thermostat. After completion of the experiment, the reaction products were "quenched" by transferring the ampoule from a thermostat into a metallic ring cooled with liquid nitrogen. During this stage the ampoule was cooled in 3-4 min to 150°, at which temperature dimerization ceases [11]. Butadiene was then determined in the presence of its dimer as described above.

Dimerization of butadiene in the gaseous phase is a homogeneous bimolecular reaction and conforms to an equation of the velocity constants of the second order [11-13]. The rate at which butadiene dimerizes at temperatures from 170 to 390° has been studied in greater detail by Kistakowsky and Ranson [11]. Assuming that the velocity constants of the dimerization of butadiene at 250 and 260° are 1.2 and 2.2 $cm^3 mole^{-1} sec^{-1}$, respectively [11], and knowing the initial butadiene concentration and the reaction time, the final butadiene concentration was calculated by means of a second order equation for the velocity constants (see the table).

A comparison of the final amounts of butadiene, calculated and experimentally determined, indicates that the presence of butadiene dimer does not affect the results of the photometric determination of butadiene.

SUMMARY

A photometric method for the determination of small amounts of butadiene suggested by N. A. Isakova has been checked and modified. It has been shown that it is possible to determine small amounts of butadiene in the presence of butadiene dimer, n-hexane, or n-heptane. The mean probable error of a single determination is ±7%.

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THE USE OF MAGNESIUM METAL IN THE DETERMINATION OF THE ALKALI METALS

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On heating organic materials containing halogens, sulfur, nitrogen [1], phosphorus [2], carbon [3], and arsenic [4] with magnesium, halides, sulfides, nitrides, phosphides, and arsenides are formed, respectively. In these compounds nitrogen, sulfur, phosphorus, halogens, and arsenic can be readily determined. Magnesium can be used for qualitative inorganic analysis [5].

The present article is devoted to a description of a method for the quantitative separation of the alkali metals which is based on their reduction with powdered magnesium on heating.

Essentially, the new method for separating and quantitatively estimating the alkali metals reduces to the following: an accurately weighed aliquot of the inorganic material containing alkali metals is mixed with excess powdered magnesium in a stainless steel test tube and the mixture heated at 650-700° for 20-25 min. The air is removed from the tube prior to commencement of the heating. When the reaction is complete, the alkali metals which have been liberated as the free elements are extracted with ethanol and they are subsequently determined titrimetrically or gravimetrically.

TABLE 1

Test material	Alkali metal, %					
	titrimetric method			gravimetric method		
	calc.	found	difference	calc.	found	difference
Na_2SO_4	32,37	32,12	−0,25	43,65	43,52	−0,13
		32,24	−0,13	46,70	46,59	−0,11
Na_3PO_4	42,02	42,16	+0,14	45,35	45,30	−0,05
		41,99	−0,08	28,46	28,38	−0,08
$Na_2B_4O_7 \cdot 10H_2O$	12,05	12,04	−0,01	19,75	19,72	−0,03
		12,06	+0,01	21,74	21,80	+0,06
$NaC_2H_3O_2$	28,02	27,80	−0,22	31,85	31,76	−0,09
		27,98	−0,04	33,07	33,02	−0,05
K_2CrO_4	40,26	40,05	−0,21	49,48	49,40	−0,08
		40,18	−0,06	64,60	64,52	−0,08
$K_2C_2O_4 \cdot H_2O$	42,44	42,34	−0,10	63,01	63,00	−0,01
		42,57	+0,13	56,47	56,40	−0,07
KH_2PO_4	28,73	28,60	−0,13	45,81	45,69	−0,12
		28,72	−0,01	42,70	42,80	+0,10

TABLE 2

Test material	Sample wt., mg	Alkali metal					
		titrimetric determination			gravimetric determination		
		amt. of 0.05 N acid, ml					
		calc.	found	difference	calc.	found	difference
Total K_2SO_4 / Na_2CO_3	57,60 / 44,30 / 101,90	29,90	29,92	—0,02	116,90	116,83	—0,07
Total Na_2SO_4 / $K_2C_2O_4 \cdot H_2O$	52,10 / 26,30 / 78,40	20,30	20,36	+0,06	76,97	76,93	—0,04
Total K_2SO_4 / Na_2SO_4	23,50 / 26,40 / 49,90	12,80	12,80	—	49,90	49,80	—0,10
Syenite No. PS* 5,05% K	196,30	10,74	10,54	—0,20	41,22	41,25	+0,03
3,18% Na	119,50	7,18	7,10	—0,08	25,35	25,31	—0,04
Syenite No. 271 * 3,75% K	139,80	5,10	5,00	—0,10	20,45	20,40	—0,05
2,00% Na	153,25	5,58	5,55	—0,03	22,27	22,31	+0,04
Syenite No. 1050* 7,33% K	149,05	9,48	9,45	—0,03	25,70	25,74	+0,04
3,02% Na	152,10	9,68	9,60	—0,08	26,25	26,26	+0,01
Syenite No. VS* 8,00% K	114,50	6,88	6,84	—0,04	28,26	28,35	—0,09
2,22% Na	104,10	6,24	6,14	—0,10	26,37	26,30	—0,07

*Results of analyses carried out at the laboratory of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry.

TABLE 3

Test material	Alkali metals, %					
	titrimetric determination			gravimetric determination		
	calc.	found	difference	calc.	found	difference
Glass 55/134	15,59	15,43	—0,16	15,59	15,37	—0,22
15,59% Na_2O **	15,59	15,32	—0,27	15,59	15,42	—0,17
Glass 279/747	15,55	15,55	0,00	14,93 *	14,95	+0,02
13,86% Na_2O ** 1,64% K_2O	15,55	15,40	—0,15	14,93 *	15,12	+0,19
Glass 75/208	15,26	15,20	—0,06	15,26	15,19	—0,07
15,26% Na_2O **	15,26	15,44	+0,18	15,26	15,00	—0,26
Glass 113/445	15,76	15,75	—0,01	15,76	15,87	+0,11
15,76% Na_2O **	15,76	15,70	—0,06	15,76	15,86	+0,10
Glass 240/1173	15,15	15,02	—0,13	15,15	14,85	—0,30
15,15% Na_2O **	15,15	15,08	—0,07	15,15	14,95	—0,20

*Calculated in terms of Na_2O.

**Standard samples. Results of analyses carried out at the Scientific-Research Glass Institute.

Experimental procedure. The test material (0.05-0.30 g) is introduced into a stainless steel test tube (200 mm long, 10-12 mm in diameter) containing a small amount of powdered magnesium (40-50 mg) Some more magnesium (400 mg) is then introduced into the tube and the contents carefully mixed. In order to avoid undesirable formation of magnesium nitride the air is expelled from the tube either by means of a vacuum pump or by some ether, 0.5-1 ml of which is introduced into the tube. The contents of the tube are then heated for 20-25 min at 650-700°.

Fifty percent alcohol is added in small portions into the cooled tube and the reaction mass broken up with a metal rod. The tube is gently warmed and the solution filtered through a No. 2 porous glass filter. These operations are carried out 10-12 times. The precipitate on the filter is given an additional wash with a small amount of alcohol. The total volume of the wash solution should not exceed 120-150 ml. The alkali metals contained in the filtrate are titrated with 0.1 N sulfuric acid using methyl red as indicator.

In order to determine the alkali metals gravimetrically, the titrated filtrate is evaporated in a beaker to a volume of 5-10 ml; the solution is then transferred to a platinum basin in which it is acidified with 2-3 drops of of concentrated H_2SO_4 and then evaporated to dryness. The alkali metal sulfates are calcined in a muffle oven at 600-650° to constant weight.

Various chemically pure compounds of the alkali metals were analyzed; they included sulfates, phosphates, oxalates (Table 1),etc., as well as mixtures of the compounds indicated (Table 2). In addition, several samples of ores (syenites) containing the alkali metals (Table 2) and glass were analyzed (Table 3).

SUMMARY

A simple, rapid, and accurate method has been developed for the quantitative separation of total alkali metals which is based on their reduction with powdered magnesium. The method does not require any expensive or difficultly available reagents or complex apparatus. A single determination takes 40-45 min.

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*Original Russian pagination. See C. B. translation.

QUANTITATIVE DETERMINATION OF ZINC IN SOILS BY A SPECTROGRAPHIC METHOD

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The methods which are widely used at present for the spectrographic analysis of metallometric samples [1] are not always satisfactory with respect to sensitivity and accuracy.

We have developed a variant of the method for the direct spectrographic determination of thousandths of a percent of zinc in soils by distilling the zinc from a hollow in a special small electrode. The probable error of a single determination is 8%. The zinc content of the soils is calculated by the three standards method, using a curve relating $\log I_{Zn}/I_{Cd}$ to $\log C$.

In contrast to electrodes described in the literature [2-4] the hollow electrode which we used was made from fine spectrographic carbon and was designed to hold 100-150 mg.

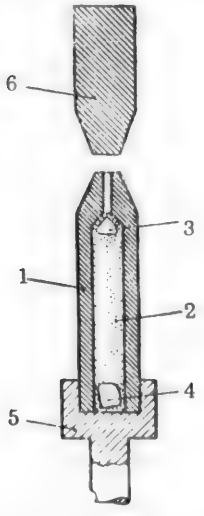

Fig. 1. Shape and position of the electrodes. 1) Electrode; 2) test material; 3) plug of wadding for preventing sputtering of sample; 4) wadding stopper; 5) electrode holder; 6) upper electrode.

The spectra were excited in an activated ac current with a strength of 12 a. The arc served at the same time for heating the lower electrode containing the test sample and for exciting the spectra.

During arc burning, an iodide reducing atmosphere was created in the electrode; the zinc compounds in the solid were converted in this atmosphere into readily volatile zinc iodide. For this purpose the test sample and standards were mixed 1 : 1 with carbon powder containing 10% cadmium iodide, the cadmium in which served as an internal standard at the same time.

The effect of the bulk composition of the samples on the relative intensity of the analytical lines was established. Accordingly, standard powders were prepared on a base similar in composition to that of the test soils. The zinc present in the chosen base was determined by the method of additions [5]. Zinc was added to the standards in the form of its oxide. Samples whose zinc content is fairly accurately known and which at the same time covers the requisite concentration range can also be used as standards.

The hollow electrodes were prepared from normal spectrographic carbon rods with a diameter of not less than 6.3 mm. The total length of the electrode was 25 mm, while the diameter of the hollow was 3.5 mm and the depth 20 mm; the diameter of the opening through which the distilled gases passed was 1 mm. The shape of the electrodes and their position with respect to each other are shown in Fig. 1.

TABLE 1

Analytical lines	Potential		Concentration range of Zn determined, %	Error of a single determination, %
	Excitation of the lines, ev	Ionization of the lines, ev		
ZnI_2 3345.02	7.78	9.39	0.002-0.1	± 8
CdI_2 3133.17	7.76	8.99		
ZnI_2 3282.33	7.78	9.39		
CdI_2 3133.17	7.76	8.99	0.005-0.3	± 8

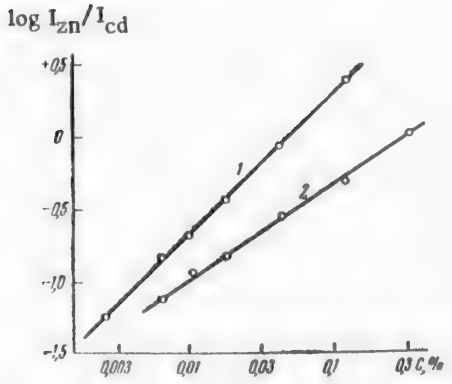

Fig. 2. The relation between the relative intensities of zinc and cadmium lines and the zinc concentration of the soil. 1) ZnI_2 3345.02 and CdI_2 3133.17; 2) ZnI_2 3282.33 and CdI_2 3133.17.

TABLE 2

Zn found, %			
spectrographic method	chemical method	spectrographic method	chemical method
0,12	0,14	0,019	0,020
0,12	0,12	0,021	0,021
0,016	0,018	0,012	0,011
0,014	0,015	0,014	0,013
0,089	0,070	0,018	0,018
0,010	0,012	0,006	0,008
0,015	0,015	0,006	0,004

The spectra of the standards and soils were photographed on "Spectrographic Type I" plates with a sensitivity of 0.8 GOST units, using an ISP-28 average dispersions spectrograph and a slit width of 0.015 mm. The slit was illuminated by means of a three-lens system of condensers, in which the height of the opening of the intermediate diaphragm used for isolating the central section of the arc flame was 1.2 mm.

In order to carry out an analysis, an aliquot of 200 mg of the air-dry soil was mixed with 200 mg of the working mixture (carbon powder and CdI_2 in the proportion of 9 : 1) and carefully ground in a mortar in the presence of alcohol or ether. 100 mg of the mixture obtained was introduced into the hollow of the electrode by means of a funnel and the bottom sealed with a plug of wadding soaked with a solution of ammonium sulfate. The electrode was then firmly fixed in the electrode holder to a depth of 2-3 mm (see Fig. 1). The interelectrode distance was adjusted to 2 mm. The exposure was 30 sec.

The spectrograms were developed under the usual conditions with a standard metal hydroquinone developer.

Zinc was determined on the basis of its most sensitive line ZnI_2 3345.02. The less sensitive line ZnI_2 3282.33 can also be used. The analytical pairs of lines are given in Table 1.

Photometric measurements were made on an MF-2 microphotometer. In order to construct the characteristic curve of the photographic plate the intensities of the iron spectrum were used [5].

Typical calibration curves are shown in Fig. 2. The analytical results taken were the mean of two parallel determinations. In Table 2 are shown the results of parallel determinations of zinc in soils by spectrographic and chemical methods.

The method is in use for the series determinations of zinc in soils during biogeochemical studies. After sufficient practice one worker can carry out 10-12 determinations in a working day, including all preparative work.

SUMMARY

A method has been developed for the direct determination of zinc in soils over the concentration range 0.002-0.1% by using an iodide reducing medium in a small hollow electrode; the probable error of a single determination is ±8%

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PHOTOMETRIC DETERMINATION OF QUADRIVALENT VANADIUM WITH ACID CHROME BLUE K

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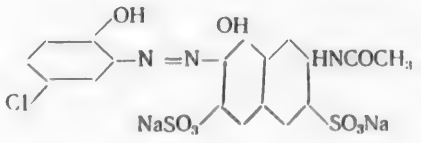
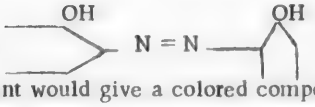
We have used acid chrome blue K, whose formula is given below, for the photometric determination of vanadium:



The presence of the group  led us to expect, in accordance with Kuznetsov's hypothesis [1, 2], that this reagent would give a colored compound with quadrivalent vanadium. In fact such a compound exists at pH 3.6-6, this compound having a maximum light absorption at 590 mμ. The optimum pH range is 4.3-5.3.

The calibration curve was constructed as follows. Two ml of vanadyl sulfate solution in 1 N H_2SO_4 was introduced into a 50 ml standard flask; to this was added an acetate buffer solution (6 ml) and 3 ml of a 0.1% solution of chrome blue K. The solution was diluted to the mark with water. The light absorption was measured on an FÉK-M photocolorimeter using a cuvette with a layer thickness of 50 mm and a green filter.

The color of solutions of the complex conforms to Beer's law over the range 0.01-0.3 μg V/ml. The experimental error is 1-3% (Table 1).

Acid chrome blue K has the highest sensitivity for quadrivalent vanadium (Table 2).

The colored compound of quadrivalent vanadium with acid chrome blue K is stable (the optical density of its solution does not change over a 24 hr period). A state of equilibrium is reached immediately on pouring the solutions together.

The presence of aluminum leads to high results for vanadium. When the amount of aluminum is 25 times that of vanadium, the relative error increases to 10%. Nevertheless, addition of tartaric acid to the solution eliminates interference from aluminum without interfering with the determination. When tartaric acid is present the relative error is not greater than 1.5% even at a ratio of Al : V = 2000 : 1. Molybdenum in ratios up to Mo : V = = 125 : 1 has almost no effect on the vanadium determinations. On increasing the molybdenum further the error becomes appreciable. Tungsten does not interfere at ratios up to W : V = 10 : 1; at higher ratios of tungsten to vanadium, the error becomes appreciable. Under the experimental conditions used, chromium is present in the trivalent state; when the amount of it present is not more than 200 times that of vanadium, it does not interfere.

TABLE 1

V taken, μg	V found, μg	Error	
		absolute	relative
2	2.06	+ 0.06	3.0
6.2	6.1	+ 0.1	1.6
12.5	12.45	− 0.05	0.4

TABLE 2

Reagent	Sensitivity, μg V/ml
Characteristic color of V^{IV}	60
Thoron	0.1
Pyrocatechol	0.05
Stilbazo	0.025
Alizarin	0.02
Acid chrome blue K	0.01

TABLE 3

V found, %	
Phosphotungstate method	With acid chrome blue K
0.50	0.48
0.23	0.22
0.009	0.0087
0.005	0.005

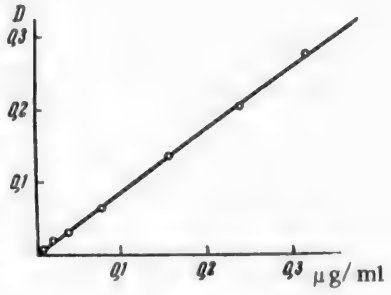


Fig. 1.

When larger amounts of chromium are present, the corresponding amounts of chromium should be added to the reference solution; this naturally assumes a knowledge of its approximate content.

Fluoride, chloride, nitrate, and phosphate ions do not interfere with vanadium determination.

Tartaric and citric acids do not interfere with vanadium determination, but slow down formation of the colored compound of quadrivalent vanadium with acid chrome blue K when the hydroxy acids are introduced prior to the dye. Thus, when citric acid is added to a solution containing 7.9 mg of vanadium, and the acid chrome blue K added afterwards, the color intensity gradually increases, but only reaches a maximum after 24 hr. When, on the other hand, the order of addition is reversed and the dye is added first, followed by the citric acid, the color is established rapidly. Oxalic acid gradually destroys the compound of quadrivalent vanadium with acid chrome blue K. Ascorbic acid does not interfere.

The following technique was used for determining the vanadium content of silicate rocks. An aliquot of 0.1-0.2 g was fused with sodium carbonate and potassium nitrate and the melt leached with water. After filtering off the precipitate of silicic acid, the filtrate was evaporated to the "moist salt" state. The "moist salts" were dissolved in 1 N sulfuric acid. The clear solution was transferred to a 25-50 ml standard flask and made up to the mark with water. To an aliquot of this solution was added 1 ml of 3% ascorbic acid solution and a few drops of formic acid; 6 ml of an acetate buffer was then added, followed by 3 ml of 0.1% acid chrome blue K solution. The volume of the solution was made up to 50 ml. All the reagents, in the same amounts as those used for the test solution, were added to the reference solution. The light absorption was measuredon an FÉK-M photocolorimeter using a cuvette with a layer thickness of 50 mm and a green filter.

The results obtained by the method suggested are comparable in accuracy to those obtained by the phosphotungstate method.

The selectivity and sensitivity of the method involving acid chrome blue K is higher, so that it is possible to work with small aliquots.

SUMMARY

It has been shown that it is possible to determine vanadium photometrically with acid chrome blue K.

The compound of quadrivalent vanadium with acid chrome blue K exhibits maximum light absorption at 590 mμ. It is formed in acid solutions; the optimum pH range is 4.3-5.3. The solutions conform to Beer's law for vanadium concentrations within the range 0.01-0.3 μg/ml. The sensitivity of the reaction is 0.01 μg/ml.

The method can be recommended for the determination of small amounts of vanadium in silicate rocks.

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A PHOTOMETRIC METHOD FOR THE DETERMINATION OF RHENIUM IN CATALYSTS

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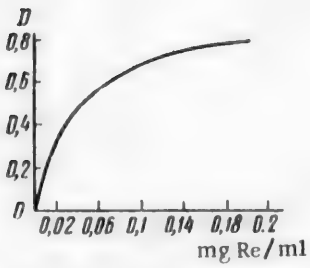
Rhenium is determined quantitatively by a gravimetric method which is based on its precipitation with nitron [1]. Rhenium can be determined photometrically as its compound with thiocyanate [2], α-furildioxime [3], thiourea [4], 2,4-diphenylthiosemicarbazide [5], methyl violet [6], stannous chloride and sodium tellurate [7], etc. Recently, the catalytic properties of rhenium-alumina catalysts have been studied [8]. We have determined rhenium quantitatively in such catalysts by the photometric thiourea method suggested by Ryabchikov and Lazarev [4].

In order to construct a calibration curve, standard solutions of the thiourea complex of rhenium were prepared containing 0.01, 0.02 and then right up to 0.2 mg Re/ml at intervals of 0.02 mg/ml. The standard solutions are prepared as follows. One g of chemically pure rhenium metal is placed in a beaker in which it is treated with 5% HNO_3 by heating until the metal has dissolved completely. The solution is transferred to a 100 ml standard flask in which it is diluted to the mark with water. The solution obtained contains 10 mg rhenium per ml. Standard solutions of the concentrations indicated above are prepared in a series of 50 ml standard flasks; appropriate amounts of the rhenic acid solution are introduced into the flasks, followed by 10 ml of concentrated hydrochloric acid, 10 ml of a 5% aqueous solution of thiourea, and 2 ml of a 20% solution of stannous chloride in concentrated hydrochloric acid; the solutions are finally made up to the mark with water and thoroughly mixed. After one hour, using an FÉK-M photoelectric colorimeter fitted with a No. 3 blue filter, and using cells in which the distance between the working surfaces is 10 mm, the optical density of the standard solutions prepared is measured relative to water. The relation between the optical density of the solutions of the rhenium-thiourea complex and rhenium concentration is shown in the diagram. The curve which we obtained is similar in character to that given in the paper by Ryabchikov and Lazarev [4].

Determination of the Rhenium Content of Rhenium-Alumina

Catalysts	Optical density	Rhenium found	
		mg in 1.00 g sample	%
Before catalysis			
5% $Re-Al_2O_3$	0.57	60	6
15% $Re-Al_2O_3$	0.75	160	16
20% $Re-Al_2O_3$	0.79	200	20
After catalysis			
20% $Re-Al_2O_3$	0.79	200	20



The relation between the optical density of solutions of the rhenium-thiourea complex and rhenium concentration.

Rhenium is extracted from the catalyst by means of 5% nitric acid; for this purpose 1.00 g of the rhenium-alumina catalyst which has been carefully ground in a mortar is treated in a glass beaker with 25 ml of 5% nitric acid by heating on a boiling water bath for 15 min; the solution is transferred to a 100 ml standard flask and is diluted to the mark with water. The solution is filtered through a No. 3 glass filter. Five ml of the filtered solution is introduced into a 50 ml standard flask; 10 ml of concentrated hydrochloric acid is added, followed by 10 ml of a 5% thiourea solution and 2 ml of a 20% solution of stannous chloride in concentrated hydrochloric acid; the solution is finally made up to the mark with distilled water. The optical density of the solution is measured after one hour, and the rhenium content determined by means of the calibration curve.

An attempt to use 30% hydrogen peroxide instead of nitric acid for extracting the rhenium-alumina catalyst was not successful.

The table contains results obtained during the determination of rhenium in rhenium-alumina catalysts.

SUMMARY

The thiourea photometric method for the determination of rhenium has been used for the determination of the latter in rhenium-alumina catalysts. Metallic rhenium is completely extracted from the rhenium-alumina catalysts by treatment of the latter with 5% nitric acid.

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*Original Russian pagination. See C. B. translation.

A COMPLEXONOMETRIC METHOD FOR THE DETERMINATION OF QUADRIVALENT URANIUM BY MEANS OF THE INDICATOR ARSENAZO I

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The method suggested in the present article for the determination of quadrivalent uranium is based on its titration with a solution of sodium ethylenediaminetetraacetate(EDTA-Na), there being no need to remove excess reducing agent.

The minimum pH value (pH_{min}) of 1.15 at which it is possible to titrate a 5×10^{-4} M solution of quadrivalent uranium complexonometrically with an accuracy of down to 0.1% was calculated by means of Yatsimirskii's equation [1] $pH_{min} = \frac{1}{4}(\Sigma pK_D - pK + 9.30)$, where ΣpK_D is the sum of the indices of the stepwise dissociation constants of ethylenediaminetetraacetic acid ($pK_1 = 2.21$ [2], $pK_2 = 2.77$ [2], $pK_3 = 6.16$ [3], $pK_4 = 10.26$ [3], $\Sigma pK_D = 21.40$) and pK is the index of the instability constant of the ethylenediaminetetraacetate of quadrivalent uranium and is equal to 26.1 [2].

In order to establish the titration end point visually, and in order to increase the selectivity of the method, it is essential to choose an indicator which forms a colored compound with quadrivalent uranium at a pH approximating to pH_{min}. It is known that arsenazo I forms a blue colored compound with thorium, the maximum yield being given at pH 1.9 [4]. By studying the interaction of arsenazo I with uranium, we established that this element also forms a blue colored compound, but the maximum yield in this case is at pH 1.7 ± 0.1. Special experiments showed that during the complexonometric titration of uranium in the presence of arsenazo I, it is only when the pH has the value indicated at the end point that there is observed the clearest change in color from blue to rose. Changes in pH on either side of 1.7 ± 0.1 lead to low results for uranium.

Reduction of a uranyl salt to quadrivalent uranium can be effected by sodium hydrosulfite or by formamidinesulfinic acid [$H_2NC(NH)SO(OH)$], also called thiourea dioxide [5]. Formamidinesulfinic acid is the most convenient to use, since its aqueous solution is more stable, while during the reduction of uranium hardly any sulfur dioxide is evolved. Experiments showed that 0.2 g of formamidinesulfinic acid in 0.25 N sulfuric acid reduces about 200 mg of uranyl on boiling.

The following reagents were used for checking the method:

1. A standard solution of uranyl nitrate containing 7.6 g of uranium per liter. The uranium content was established gravimetrically.

2. EDTA-Na purified by Bleadl and Knight's method [6]. 5×10^{-2} and 2.5×10^{-2} M solutions of EDTA-Na were prepared by taking accurately weighed amounts of the air-dry preparation. The concentration of the solutions was checked against standard thorium nitrate solution [7], while the latter was standardized against uranyl nitrate.

3. Formamidinesulfinic acid was prepared by Fischer and Hieber's method [8] modified slightly by us: a beaker containing 2 liters of 15% hydrogen peroxide was immersed in a cooling mixture (acetone and solid carbon

TABLE 1

Determination of Uranium in Solutions of its Salts in the Presence of Impurities

Taken, mg		No. of uranium determinations, n	Uranium found (mean of n determinations), mg	Mean square error	
uranium	impurities			mg	% (relative)
1,95	—	11	1,88	±0,044	±2,34
7,60	—	11	7,60	±0,099	∓1,30
38,00	—	11	37,95	±0,15	∓0,38
114,00	—	11	114,32	±0,20	±0,18
38,00	6—Fe^{3+}, 5—Al^{3+}	11	37,99	∓0,089	±0,23
38,00	12—Fe^{3+}, 10—Al^{3+}, 500—Na_2SO_4, 500—$NaNO_3$	11	37,99	±0,083	±0,22
38,00	24—Fe^{3+}, 20—Al^{3+}, 1000—Na_2SO_4, 1000—$NaNO_3$	11	38,04	±0,086	±0,23
41,62	30— Tartaric acid	4	41,56	∓0,075	∓0,18
25,15	35— Citric acid	11	25,12	∓0,087	±0,35
25,29	100— Hydroxylamine sulfate	6	25,39	±0,046	±0,18
25,29	100— Hydrazine sulfate	6	25,33	±0,073	±0,29

dioxide). 250 g of finely ground thiourea was added to the contents of the beaker in small portions (1.0-1.5 g) with stirring, care being taken to ensure that the temperature of the liquid in the beaker was within the range −10 to + 10°. The solution plus precipitate obtained were cooled until ice appeared on the beaker walls. The beaker was then withdrawn from the cooling mixture, and, after the ice crystals had disappeared, the precipitate was filtered off through a Buchner funnel; it was washed 2-3 times with water, and dried in the air. The air-dry material is stable on storage. Yield 230 g.

4. Reducing agent solution. Four g of the formamidinesulfinic acid was dissolved in 600 ml of 0.25 N sulfuric acid. The solution can be used for reducing uranium in the course of 24 hr.

5. Arsenazo I solution − 0.1% aqueous solution.

6. Thymol blue − 0.1% solution in 5% ammonia solution.

During the determination of uranium in solutions of its salts and in the presence of foreign ions, aliquots of the aqueous standard solution of uranyl nitrate were introduced into 300 ml conical flasks and solutions of the impurities, in the amounts indicated in Table 1, added. Thirty ml of the reducing solution was then added to each flask, and the whole heated to the boil and boiled for 5-8 min, the solution being thereby evaporated to a volume of 10-15 ml. Immediately prior to titration, the solutions, which had been cooled to room temperature, were diluted with 175 ± 5 ml of distilled water, a pH of 1.7 ± 0.1 being thereby obtained. One ml of arsenazo I solution was then added, and the quadrivalent uranium titrated with EDTA-Na solution with continuous stirring until the color changed from blue to a pure rose.

The method permits determination of 2-115 mg of uranium (Table 1) reliably and with reasonable reproducibility. It is best to establish the titer of the EDTA-Na solution with respect to uranium by means of a standard solution of uranyl nitrate. Al^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Mn^{2+}, Cr^{3+}, Be^{2+}, La^{3+}, Ce^{3+} (in amounts commensurate with that of the uranium) do not interfere with uranium determination; neither does tartaric acid in amounts up to 30 mg, citric in amounts up to 35, sodium sulfate in amounts up to 2 g, sodium nitrate in amounts up to 1 g, nor hydrazine sulfate and hydroxylamine sulfate in amounts up to 100 mg.

Fe^{2+} ions do not interact with EDTA-Na under the conditions we have chosen (pK FeY^{2-} = 14.33, pK FeY^{-} = = 25.1), and, in amounts of 25-30 mg, does not interfere with uranium determination. Nevertheless, when the solution is not stirred adequately during titration in the presence of iron, a localized excess concentration of EDTA-Na may develop (the compound FeY^{-} is partially formed) and the results obtained are high and the reproducibility is poor. Cu^{2+} ions on boiling with a solution of formamidinesulfinic acid are precipitated as Cu_2S; the characteristic

TABLE 2

Comparison of Gravimetric and Complexonometric Determinations of Uranium. The Number of Determinations by the Suggested Method was 11

Test material	Uranium found gravimetrically, % *	Complexonometric method		
		uranium found, % *	Mean square error	
			% absolute *	% (relative)
Uranoso uranic oxide	84.78	84.83	∓ 0.20	∓ 0.24
Uranium tetrafluoride	71.93	71.82	± 0.11	± 0.15
Sodium uranyl acetate	50.82	50.65	± 0.19	± 0.37
Uranium-aluminum alloy	67.96	68.07	∓ 0.16	∓ 0.24
Tributylphosphate solution	34.31	34.41	± 0.06	∓ 0.17
$UO_2(NO_3)_2$	31.79	31.65	± 0.08	± 0.24

*For solutions, g/liter.

color of copper sulfide interferes with observation of the end point. In the presence of 2-3 mg of copper, determination of uranium becomes impossible if the Cu_2S dissolves in the thiourea. Vanadium salts hinder the quantitative reduction of uranyl, but quadrivalent uranium can still be determined in the presence of 1-2 mg of vanadium if, prior to reduction, 2 g of sodium sulfate is added to the solution and the titration is carried out immediately after reducing the uranium.

Ions which form stable compounds with EDTA-Na (Th^{4+}, Sc^{3+}, In^{3+}, Zr^{4+}, Hf^{4+}) or with quadrivalent uranium (PO_4^{3-}, F^-, $C_2O_4^{2-}$) interfere with the determination. It should be pointed out that oxidation of quadrivalent uranium in the solutions obtained after reduction of uranyl with formamidinesulfinic acid is not observed at room temperature for 8 hr, as long as the solutions do not contain vanadium or they are not diluted with distilled water.

The optimum color change of the indicator at the end point and the highest experimental accuracy are attained on titrating 15-20 mg of uranium. Accordingly, during the analysis of solid materials containing large amounts of uranium it is expedient to carry out determinations on aliquots of the solution obtained after dissolving a large sample. The choice of the dissolution method depends on the composition of the test material. 1.0-0.5 g aliquots of sodium uranyl acetate and uranium oxides are dissolved in 10-20 ml of nitric and 5-15 ml of hydrochloric acid on heating, the solutions being then evaporated to a volume of 3-4 ml. For the analysis of uranium tetrafluoride and alloys of uranium with aluminum, 3-4 ml of sulfuric acid (1 : 1) is added in addition, and the solutions are heated until thick white fumes are given off. The solutions obtained are diluted with water (30-40 ml) and heated to the boil; they are transferred, without filtering, into 100 ml standard flasks, cooled to room temperature, made up to the mark with water, and mixed. An aliquot (15-20 mg of uranium) is transferred to a 300 ml conical flask; 2-3 drops of 0.1% thymol blue is added, followed by ammonia until the color of the indicator changes to orange-yellow (pH 2.5-2.7). Thirty ml of reducing solution is added and the procedure outlined for the determination of uranium in solutions of its salts then followed.

Determination of uranium in kerosene-tributylphosphate solutions was carried out as follows: for uranium contents of 70-10 g/liter, an aliquot (0.5-1.0 ml) was transferred directly into a 300 ml conical flask and 30 ml of the reducing solution added. For uranium contents of 0.3 to 10 g/liter, an aliquot (10-2 ml) was transferred to a 50-75 ml separating funnel, and the uranium extracted with three lots of reducing solution (10 ml in each case), and the re-extracts collected in the same size flask. The determinations were completed as described above.

The results given in Table 2 and other experiments showed that the suggested method permits uranium to be determined reliably and with reasonable accuracy in its oxides, salts, alloys with aluminum, silicon, iron, and beryllium, and also in aqueous and tributylphosphate solutions. In two hours one analyst can carry out 10-12 determinations of uranium in the solutions obtained after decomposing the test material, or after the requisite technological operations.

The authors wish to thank V. A. Golovnya and G. T. Bolotova, who supplied information on the properties of formamidinesulfinic acid and on the reduction conditions for uranium which facilitated the development of the method suggested for the determination of uranium.

SUMMARY

A complexonometric method has been developed for the determination of uranium; it is based on the reduction of uranium to its quadrivalent state by formamidinesulfinic acid with subsequent titration of the solution with EDTA-Na using arsenazo I as indicator.

The method is suitable for the determination of uranium in its salts, oxides, alloys, and in tributylphosphate and other extracts.

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SPECTROGRAPHIC DETERMINATION OF TRACES OF METALS IN HYDROGEN PEROXIDE SOLUTIONS

K. K. Popkov and L. M. Shtifman

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Original article submitted February 18, 1960

Normal techniques for the spectrographic analysis of solutions [1-2] cannot be used for the determination of traces of metals in hydrogen peroxide solutions, since on introducing such solutions into the flame of an arc or a spark turbulent evolution of oxygen occurs and the foam that is formed short circuits the interelectrode gap. Decomposition of the hydrogen peroxide by boiling it in a flask fitted with a reflux condenser takes from three to eight hours and cannot be recommended.

These difficulties can be avoided by placing a known amount of test solution containing an internal standard on a carbon electrode of special design which is heated to 70-200° (see Fig. 1). The normal type of carbon electrode is turned on a special lathe into the shape of a nail with a concave spherical head. The test solution is placed on this head. A spiral of nichrome wire is heated with a current of 12 v. The electrode is then placed in the support of the spectrograph and combustion is carried out in an ac arc. This method of preparing the sample ensures complete removal of volatile components without destroying the proportion of the metals in the dry residue. Moreover, by evaporating different amounts of test solution with an equal amount of internal standard it is possible to determine the concentration of the metals over a wide range, using for this purpose calibration curves constructed for a comparatively narrow concentration range.

Experimental procedure. Test hydrogen peroxide solution (in 0.2-1 ml lots) containing the internal standard was placed on 2-3 electrodes. The spectra were photographed on an ISP-22 or ISP-28 spectrograph with a PS-39 or DG-1 arc generator. The interelectrode gap was established at a distance of 20 cm from the slit. The current strength of the arc was 3-4 a. The photographs were taken without a condenser. Exposure time was 15 sec. The spectra were measured photometrically on an MF-2 microphotometer. Both reproducing and spectrographic plates were used for recording the spectra. The internal standard was a cobalt sulfate solution with a concentration of 200 mgCo/liter. The most suitable lines were found to be: for the lines Al 2568, Fe 2598, Fe 2599, Cr 2666, Cr 2677, the line Co 2580 was chosen; while for the lines Ni 3002, Ni 3003, Sn 3034, Cu 3247, Al 3092, the line chosen was Co 3044. Calibration curves (Fig. 2) were constructed by preparing five solutions of the chemically pure salts covering the following concentration ranges in terms of the metals: Ni, 10-300 mg/liter; Fe, 10-200 mg per liter; Sn 10-200 mg/liter; Cr, 20-200 mg/liter; Cu, 0.2-3 mg/liter; Al 10-1000 mg/liter. The solutions were acidified with sulfuric and hydrochloric acids.

Because the chosen analytical pairs of lines were not sufficiently homologous, particular attention was given to third element effects and to ensuring that the chosen conditions were rigorously observed.

The presence of Na and K in solution at concentrations less than 1 g/liter does not affect the accuracy and sensitivity of the determination, but at a concentration of 5-10 g/liter of these elements the sensitivity of the determination of all the metals decreases 10-20 times, while the relative error in the determination of Cu, Al, and Cr amounts to 50% and in the determination of Fe to 20-30%. Accordingly, where it is known beforehand that the H_2O_2 solution contains significant amounts of Na and K, analysis of these solutions should be carried out on the basis of standard solutions, to which the appropriate amounts of potassium and sodium salts have been added. Organic

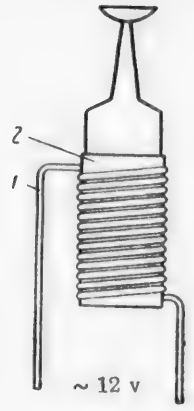

Fig. 1. Carbon electrode with heater. 1) Nichrome wire spiral, diameter 0.5 mm; 2) mica insulation.

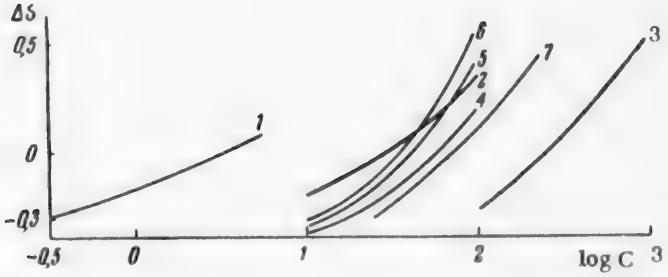

Fig. 2. Calibration curves. 1) Cu 3247; 2) Al 3092; 3) Al 2568; 4) Sn 3034; 5) Fe 2599; 6) Ni 3002; 7) Cr 2666. The difference in blackening $\Delta S = S_x - S_{Co}$ is plotted along the ordinate.

compounds are almost completely removed after placing the samples on the electrode and heating them to 300-400° in the same nichrome spiral. Incompletely burnt organic materials lower the sensitivity of the determination of impurities, on an average, by one order.

The method described permits determination of from 0.1 to 1000 mg/liter of iron, nickel, chromium, tin copper, and aluminum in hydrogen peroxide solutions. The relative mean square arithmetic error is 10-15%. During analysis of solutions containing less than 0.5 g/liter of K and Na, the relative error drops to 5%. Three parallel determinations are carried out and the mean taken. Analysis of one sample takes about one hour.

SUMMARY

A spectrographic method is described for the determination of nickel, iron, tin, chromium, copper, and aluminum in hydrogen peroxide solutions; it covers the range 0.2-3 mg/liter in the case of copper, and 10-1000 mg/liter for the remaining elements. The hydrogen peroxide is evaporated on a heated graphite electrode of special design. The part of the electrode containing the dry residue is completely burnt in an ac arc.

Cobalt lines are used as the internal standard. Cobalt is introduced into the hydrogen peroxide beforehand.

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REVIEW AND BIBLIOGRAPHY

T. A. KRYUKOVA, S. I. SINYAKOVA, AND T. V. AREF'EVA

POLAROGRAPHIC ANALYSIS. Goskhimizdat, 1959, 772 pages. 5,000 printed. Price 34 rubles, 50 kopecks.

Reviewed by A. G. Stromberg

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 1, pp. 115-117, January-February, 1961

The book is the first Soviet monograph on polarography,* one of the objects of this book being the bringing together of the contributions of Soviet research workers to polarography. Foreign textbooks [1-10] do not deal in sufficient detail with the work of Soviet polarographists. Only individual problems in polarography have been considered in Russian monographs [11-14]

The book consists of five parts; it contains 26 chapters, supplemental information, and an appendix. References to the literature are given at the end of each chapter. About 2,500 references are given. At the beginning of the book a list is given of the basic textbooks and reviews on polarography and its individual branches.

The first part (Chapters I-IV, 165 pp., 504 references) is devoted to a consideration of the theoretical and experimental bases of polarography.

Modern ideas and rules of electrochemistry are considered in the first chapter (the double electrical layer, null charge potential, the theory of concentration polarization and convection diffusion, the effect of potential on the adsorption of surface-actice materials on the mercury electrode, the concept of ψ' potentials, etc.). Unfortunately, this chapter does not deal with modern ideas on the kinetics of electrode processes developed by A. N. Frumkin, et al. (the concept of the exchange current, transport coefficient, the slow discharge – ionization theory, etc.).

The second chapter is devoted to an exposition of the fundamental theoretical basis of polarography. Here is treated in particular detail, and this is very valuable, the theory of maxima on polarographic waves and the mechanism of the inhibition of tangential movements of mercury by surface-active materials, which has been developed almost exclusively by Soviet workers, in particular, by one of the authors of the book (T. A. Kryukova). These questions are treated incompletely and inaccurately in foreign monographs. Fairly detailed consideration is also given in this chapter to the theory of the effect of various factors on the diffusion current, the theory of the charge current, the theory of catalytic waves, and some other theoretical questions. About 400 references are given to the literature on polarographic theory.

The introduction of more detailed consideration of some theoretical problems in polarography (derivation of equation for the diffusion current and for polarographic maxima) into the "Supplement" at the end of the book is a good idea.

There are, however, serious gaps in the exposition of the theory of polarography. Completely inadequate attention has been given to the theory of reversible and irreversible polarographic waves. Equations for various

*The importance attached to polarography in recent years is illustrated by the award of a Nobel prize for chemistry to the famous Czech scientist, Ya. Heyrovsky, who discovered and developed the polarographic method.

reversible waves have not been derived (in solutions of simple and complex ions, during overcharging of ions, for organic materials). The application of polarography to the study of complex compounds is treated very incompletely. In particular, there is no information on De Ford and Hume's method for calculating the composition and instability constants in the presence of several equilibrium complexes in solution. Almost nothing is said about the theory of irreversible and kinetic polarographic waves, a theory which has been considered in detail in the last ten years in a number of papers (see,e.g.,[10]). It is true to say, however, that these questions have received some attention in chapter XXIV (amalgam polarography).

The third chapter contains a lot of new and original material on the effect of various factors on the functioning of the dropping mercury electrode. Valuable information is also given about other electrodes which have been finding ever wider application in polarography. The drawback of this chapter is the absence of a clear distinction between the two main types of operation of the dropping mercury electeode: 1) in practical analytical work, in which surface-active materials (gelatin) are added; and 2) in certain special cases which are encountered in physicochemical studies where it is necessary to obtain a normal diffusion current on a dropping mercury electrode in the complete absence of any surface-active materials. Most of the complications which are met during work with a dropping mercury electrode and which are noted in this chapter (richly illustrated with experimental material obtained by the author) relate precisely to this second case and are of no great importance in practical work when surface active materials (0.002-0.01% gelatin) are added to the solution.

The fourth chapter contains valuable information on the construction of modern polarographs and polarographic electrolyzers, and also on the technique of polarographic investigation.

The second part of the book (Chapters V-XIII, 225 pp., 511 references) is devoted to the application of polarography to the analysis of inorganic materials. The material on the polarography of the various elements is systematized into eight chapters, in accordance with the number of groups in the Mendeleev periodic system. The polarography of anions and molecules is treated separately in the thirteenth chapter. After a description of the polarographic properties of a given element in various supporting electrolytes, determination of this element in various technical and natural materials is discussed. First of all a general description of the technique is given, the requisite reagents and solutions are then listed, and finally the experimental procedure is described in detail. This part of the book is a very useful practical textbook for workers in chemical laboratories who use polarography for the analysis of various materials. Soviet literature on the polarography of inorganic compounds (up to 1955-1956) is very fully treated in this section, and the work of foreign workers is also covered. It should be pointed out that the authors of this part of the book (S. I. Sinyakova and T. V. Arefeva) have themselves many years' experience in developing polarographic techniques for the analysis of mineral raw materials and nonferrous mineralogical products.

The use of polarography in the analysis of organic compounds is the subject of the third part of the monograph (Chapters XIV-XVIII , 108 pp., 296 references). After a discussion of some general questions in the polarography of organic compounds (chapter XIV), the four succeeding chapters are devoted to the polarography of various groups of organic compounds, on the same plan as that adopted for polarographic compounds. Nevertheless, the literature on the polarography of organic compounds* (particularly foreign) is treated far less fully than that on the polarography of inorganic compounds.

The fourth section of the book (Chapters XIX XXII, 67 pp., 125 references) considers the general principles (Chapter XIX) and individual techniques of amperometric titration. Recently O. A. Songina's monograph on amperometric titration [11] was published, and the literature on this question was dealt with much more fully there (427 references).

The fifth part of the book (Chapters XXIII-XXVI, 32 pp., 84 references) is devoted to various other questions in polarographic analysis: adsorption analysis, amalgam polarography, derivative, differential, and oscillographic polarography. These special divisions of polarography have been finding increasing significance in recent years. Thus, amalgam polarography on a stationary mercury drop at a constantly changing potential and oscillographic polarography permit determination of some elements at concentrations of 10^{-7}-10^{-8} M. It is a pity therefore that the authors of the monograph have given such little space to these new branches of polarography.

*To have an idea of the volume of literature on the polarography of organic compounds, one can cite Wawzonek's review [15], in which 500 references are given covering three years (1955-1957).

Tables are given in the appendix which contain the half-wave potentials of inorganic compounds (about 1000 values) and organic compounds (about 800 values). Opposite each half-wave potential is given the literature reference, a list of which is given at the end of the tables. (Bibliography, 636 references). Of great value are the polarographic spectra of the elements in fifteen supporting electrolytes (pp. 726-727). These spectra can be used for choosing the requisite supporting electrolyte for the analysis of a given mixture of elements.

It can be said that the authors have compiled a valuable book which can serve as a means for making one's acquaintance with the theoretical bases of polarography and as a textbook in carrying out polarographic determinations during the analysis of complex inorganic and organic materials. It only remains to deplore the fact that such a small edition has been published (5,000); this will not be enough to satisfy the large demand there will be for it.

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CURRENT EVENTS

CONFERENCE ON KINETIC METHODS OF ANALYSIS

(JUNE 14-16, 1960, Ivanovo)

V. P. Vasil'ev, V. D. Korableva, and K. B. Yatsimirskii

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January-February, 1961

At the conference on kinetic methods of analysis, 16 reports were presented by workers at the Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR; the Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian SSR; Moscow, Kiev, and Dnepropetrovsk Universities; the Ivanovo Chemico Technological Institute; and the Institute of Chemical Reagents (IREA). Representatives of a number of colleges, scientific-research institutes and factory laboratories, as well as chemists from Ivanovo, took part in the work of the conference.

The following reports were read and discussed: I. P. Alimarin and Yu. V. Yakovlev, "The Possibilities of Modern Methods for the Determination of Ultra Small Amounts of Impurities in Super Pure Materials"; K. B. Yatsimirskii, "The Modern State and Perspectives of the Development of Kinetic Methods of Analysis"; A. K. Babko and L. V. Markova, "The Photometric Determination of Micro Amounts of Sulfides and Sulfur in Metals on the Basis of their Catalytic Action on the Iodine-Azide Reaction"; B. E. Reznik and N. V. Pchelkin, "The Photometric Determination of Copper and Molybdenum on the Basis of their Catalytic Action"; B. E. Reznik, G. M. Ganzburg, and N. A. Bednyak, "A Study of the Catalytic Action of Certain Transition Elements on the Reduction of Molybdenum by Thiocyanate"; R. P. Pantaler, "A New Kinetic Method for the Determination of Traces of Tungsten and Molybdenum"; L. T. Bugaenko, "The Use of the Kinetic Method of Analysis in Radiation-Chemical Studies"; S. I. Sinyakova, "A Review of the Use of Kinetic (Catalytic) Currents in Polarography for the Determination of very Small Amounts of a Number of Elements"; K. B. Yatsimirskii and L. I. Budarin, "Determination of Equilibrium Constants in Systems Involving Complex Formation on the Basis of a Study of Catalytic Polarographic Currents"; V. I. Kuznetsov and E. S. Ul'yanova, "Radiation-Kinetic Determination of Polonium"; L. I. Budarin and K. E. Prik, "New Types of Apparatus for Kinetic Methods of Analysis"; M. N. Orlova, "Kinetic Methods of Determining Silver in Solution"; A. K. Babko and N. M. Lukovskaya, "The Effect of Complexing Agents on the Catalysis of Chemiluminescence Reactions"; L. P. Raizman, "A Study of Complex Formation between Zirconium and Organic Acid Anions by a Kinetic Method"; K. E. Prik, "The Application of the Kinetic Method to the Study of Complex Formation of Sexivalent Molybdenum in Solution"; and M. B. Shustova, "The Determination of Vanadium in Titanium Metal."

Lively exchanges of opinion followed the reports. The conference showed that work on kinetic methods of analysis is now being successfully carried out in many cities (Moscow, Kiev, Ivanovo, Dnepropetrovsk, Khar'kov, and Odessa). The most important lines followed by these studies were indicated. It was pointed out that it is necessary, on the basis of results already obtained, to go over to developing actual analytical techniques for practical use. One of the most important lines of research is to clarify the mechanisms of the catalytic reactions in use; a fuller study of their kinetics is possible. Of very great interest is the search for the connection between the various physicochemical characteristics of catalyst particles and their catalytic activity. The existence of a profound mutual connection between the problem of complex formation and the reaction kinetics in solution was demonstrated at the conference.

In order to carry research further in the field of kinetic methods of analysis it is necessary to develop new types of apparatus and to bring them into production; to issue special samples and standard materials whose content of micro impurities has been definitely established; reagents of particularly high purity are also required. It is desirable that reviews and monographs be published on kinetic methods, and that the links between research workers in this field, both in this country and beyond it, be strengthened.

FIFTH CONFERENCE ON THE ANALYSIS OF THE NOBLE METALS

(SEPTEMBER 20-23, 1960, Novosibirsk)

O. E. Zvyagintsev

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 1, p. 119,
January-February, 1961

The Fifth Conference on the Analysis of the Noble Metals was convened by the Institute of Inorganic Chemistry of the Siberian Branch of the Academy of Sciences, USSR, and the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, in conjunction with the Ministry of Finance, USSR, and the Council of National Economy of the Novosibirsk Economic Region. One hundred and twenty eight participated in the conference; they came from 18 cities in the USSR and represented 42 organizations: scientific-research institutes, higher education establishments, industrial enterprises, and state institutions. The conference heard and discussed 30 reports presented both by scientific workers and by factory workers and demonstrated the close connection between scientific and engineering forces.

K. B. Yatsimirskii (Ivanovo) gave a review on "The Use of Kinetic Methods for the Determination of the Noble Metals." In this report, in conjunction with M. N. Orlova, he gave an account of the concrete application of the measurement of the rates of certain reactions for determination of gold and silver in solution.

I. T. Filenko and I. Ya. Baulina reported on an approximate method for the determination of the composition of gold native ores without damaging them. N. S. Balandina and G. G. Kalyuzhina (Novosibirsk) reported on some techniques which they have developed for separating impurities from normally refined gold, and for preparing very pure gold by ether extraction. The total amount of impurities in such gold is not higher than 0.0001%.

V. P. Khvostova from the firm of V. M. Peshkova and V. I. Shlenskaya (Moscow) reported on the analytical use of the reaction of palladium with potassium thiocyanate, and its study by a spectrophotometric method.

A. T. Pilipenko and I. P. Sereda reported on the use of selenourea for the colorimetric determination of osmium and rhenium without their preliminary separation.

V. N. Alyanchikova, L. V. Karpova, A. D. Dut'ko, and G. V. Ryseva (Krasnoyarsk) reported on the use of spectrophotometry, photocolorimetry, and amperometry for the determination of platinum, rhodium, iridium, and ruthenium without separating them.

Three reports were devoted to spectrographic analysis, those of: V. L. Ginzburg (Moscow), "Spectrographic Analysis of Tellurium for its Content of Noble Metals"; V. P. Khrapai (Novosibirsk), "Spectrographic Methods of Analysis in the Determination of Impurities in High Purity Gold"; A. D. Dut'ko and N. I. Pankratova (Krasnoyarsk), "Spectrographic Analysis of Platinum, Palladium, and Ruthenium of High Purity."

Several reports were given by workers in the analytical laboratory of noble metals in the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR (Moscow), on work carried out under the direction of N. K. Pshenitsyn: K. A. Gladyshevskaya and L. M. Ryakhova, "The Separation of Rhodium and Iridium by Ion Exchange using the Complex Compounds of these Metals with Pyridine"; N. A. Ezerskaya, "New Polarographic and Amperometric Methods for the Determination of Ruthenium in the Form of Sodium Hexachlororuthenate"; N. N. Chalisova, "Methods of Separating Selenium and Tellurium during the Analytical Separation and Determination of Platinum Group Methods"; S. I. Ginzburg, "New Methods for the Determination of Noble Metals in Copper and Nickel Slags and in Platinum Concentrates."

A group of research workers from Kishinev – M. G. Bardin, et al. – gave a report on the polarographic determination of noble metals on a rotating platinum microdisc electrode.

V. A. Oborinskaya (Novosibirsk) reported on the use of an electrometric method for the analysis of gold-silver alloys using a chromate-silver electrode.

Two reports were given by representatives of the Noril'sk Mining-Metallurgical Combine: V. S. Belokopytov gave a review of assay-spectrographic methods of analysis, while Comrade Kashlinskaya gave a report on the chemical methods used in the combine.

The report of N. N. Maslenitskii and A. V. Polievskii (Leningrad) dealt with assay analysis for gold and silver in materials containing large amounts of iron and chromium oxides.

S. M. Anisimov, A. P. Osipov, and A. I. Chernova (Ordzhonikidze) reported on methods they have developed for the determination of small amounts of rhodium, ruthenium, and iridium by means of assay melts, and on further analysis by spectrographic and photocolorimetric methods.

A. S. Artemov gave some brief information on the work of the assay group of the central laboratory of the Irtyshskii Polymetallic Combine.

I. D. Fridman (Moscow) dwelt on the loss of gold and silver in cemented drops, which is of importance for assay laboratories.

The last report to be read was that of S. K. Shabarin (Moscow): "Notes on the History of the Art of Assaying in Russia (XVI-XIX centuries)."

The conference adopted a resolution which indicated the main lines of further work on the analysis of noble metals. It was particularly emphasized that it is necessary to renew work on sampling technique on materials containing noble metals, and on the mechanization and automation of sampling processes

It was decided to hold the next (sixth) conference on the analysis of the noble metals in Krasnoyarsk in 1963.

YU. A. KLYACHKO
(On his Fiftieth Birthday)

Recently Professor Yu. A. Klyachko celebrated his fiftieth birthday.

Yurii Arkad'evich Klyachko started his scientific and teaching activity at the beginning of the thirties, during the beginning and turbulent development of Russian science and industry. Until 1939 Yu. A. Klyachko worked in a factory and at the same time carried on with his teaching work. Much of his work on colloidal phenomena in metals relates to this period. In the field of analytical chemistry Yurii Arkad'evich gave most of his attention to developing methods for the determination of gases and inclusions in light metals.

In the post war period, Yu. A. Klyyachko developed the questions of the application of the periodic law in analytical chemistry, and the theory of precipitation formation.

Much of the work of Yurii Arkad'evich has been devoted to the physicochemical study of processes which occur during the analysis of gases in metals, and also during the anode dissolution of alloys, for the purpose of their phase analysis. Yu. A. Klyachko has devoted particular attention to the origin and behavior of hydrogen in metals. He has contributed a great deal to the development of analytical apparatus.

Yurii Arkad'evich has written the following books: "Oxidimetry" (in collaboration with L. V. Timofeev); "A Course in Qualitative Analysis" (in collaboration with S. A. Shapiro); and "The Analysis of Gases and Inclusions in Steel."

Yu. A. Klyachko has always been distinguished by intense energy and his huge capacity for work. In 1933 he took an active part in editing the journal "Zavodskaya Laboratoriya"; in the D. I. Mendeleev All-Union Chemical Society; the Commission on Analytical Chemistry, Academy of Sciences, USSR; and in the work of the editorial boards of a number of journals and publishing houses.

He has written more than 150 scientific papers.

We wish Yu. A. Klyachko new creative successes, health, and many years of fruitful labor.

The Commission on Analytical Chemistry
Academy of Sciences, USSR

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.– Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

THE STRUCTURE OF GLASS

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